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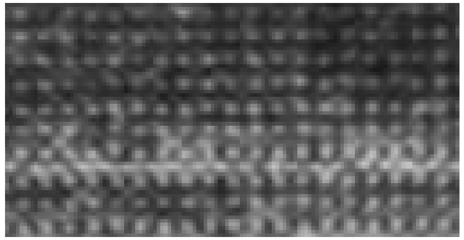
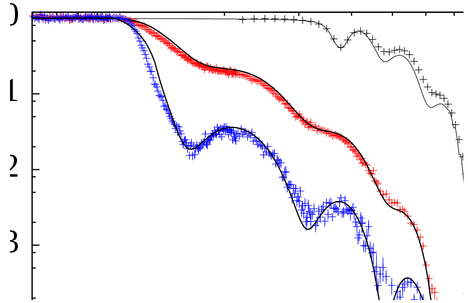
introduction to reflectometry thin films and hetero structures

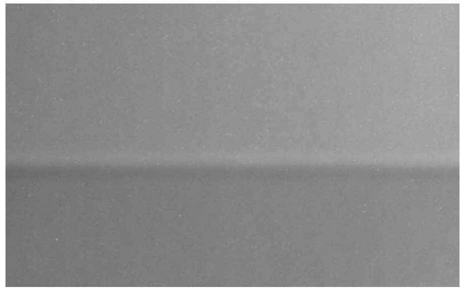
PSI summer school on condensed matter research
Zug, 11. – 17. August 2012
Imaging Life and Matter - using photons, neutrons and muons

outline

- heterostructures
  - → magnetic layers
  - → membrane systems
- reflectometry
  - → (few formulae)
- . . . derivation
  - → (lots of formulae)
- experimental examples
  - → Fe/Si
  - → FeSi/GaAs interfaces
  - → bio-membrane
- relevance for imaging
  - → YES, there is some!







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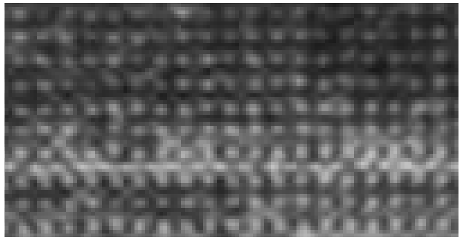
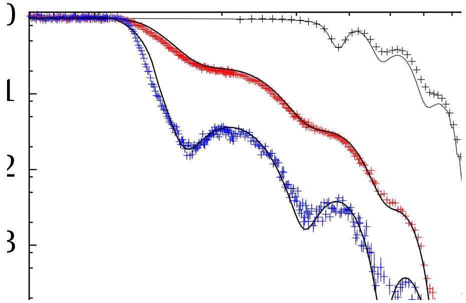
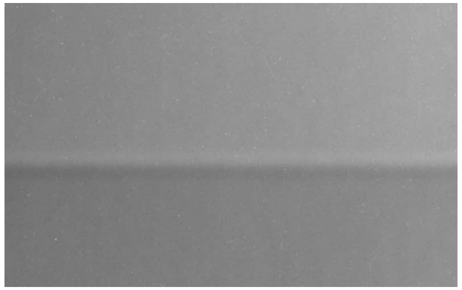
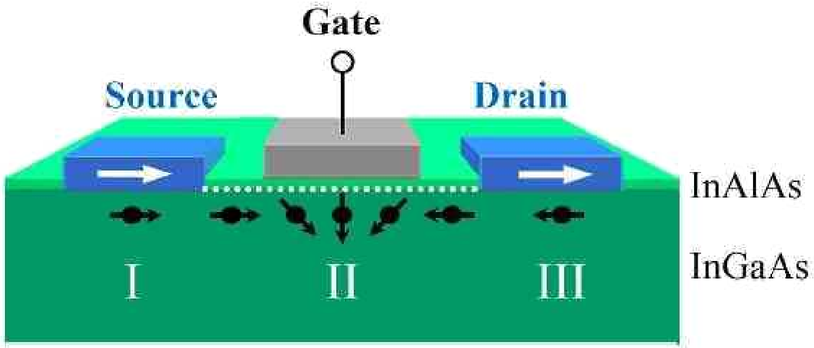






. . . the damn magnetically dead layers . . .

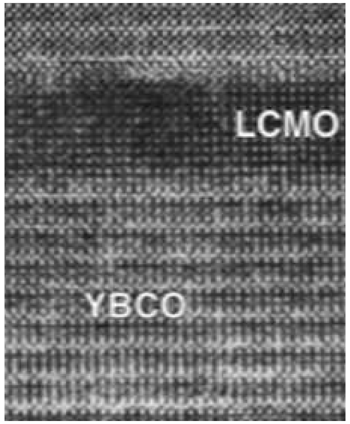
• down-scaling ⇒ thin magnetic films
e.g. magnetic data storage



• spin polarised electron injection
e.g. spin-injection in a spin-transistor

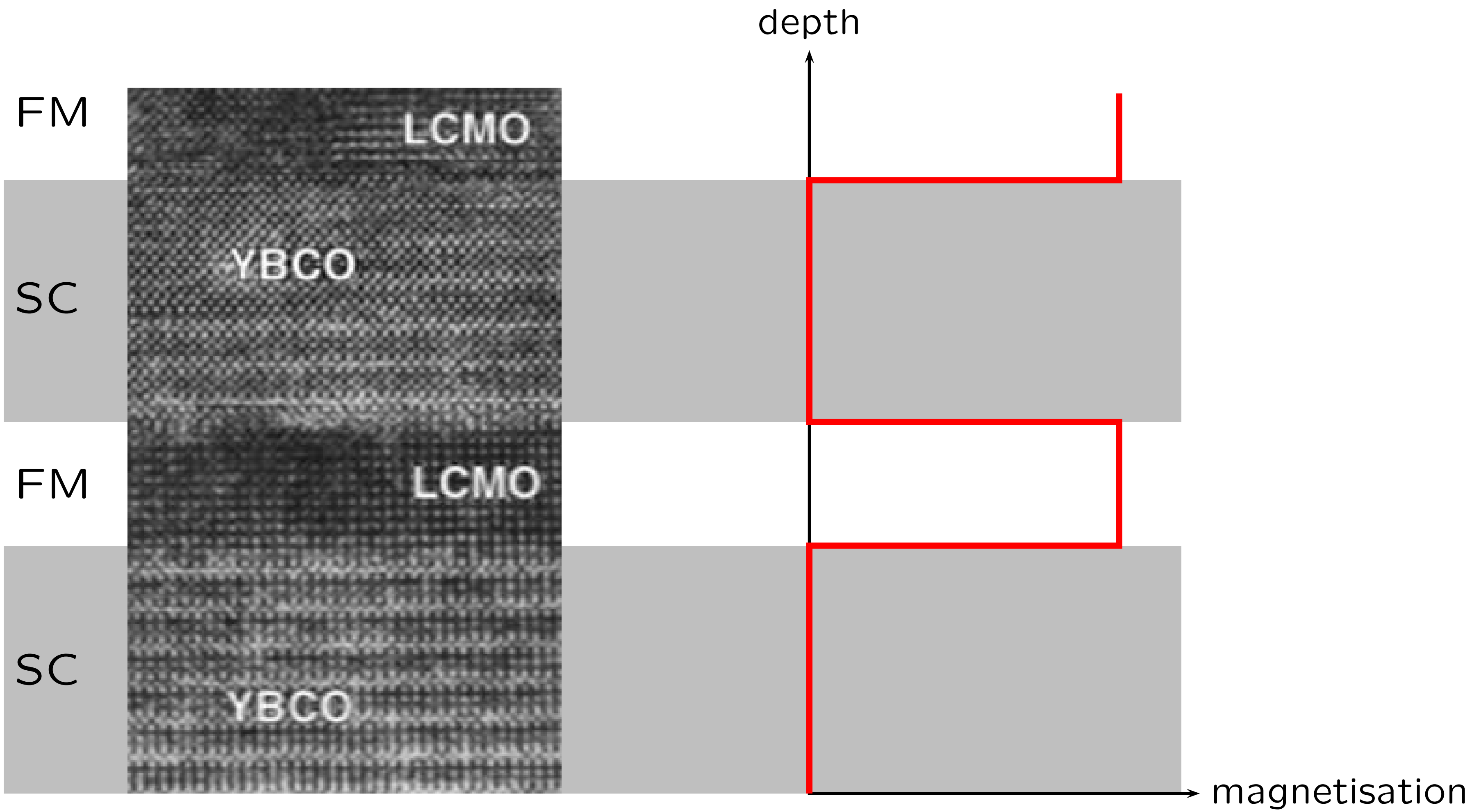
• conflicting properties at interfaces

e.g. interface $\dfrac{\text{ferro} - \text{magnet}}{\text{superconductor}}$



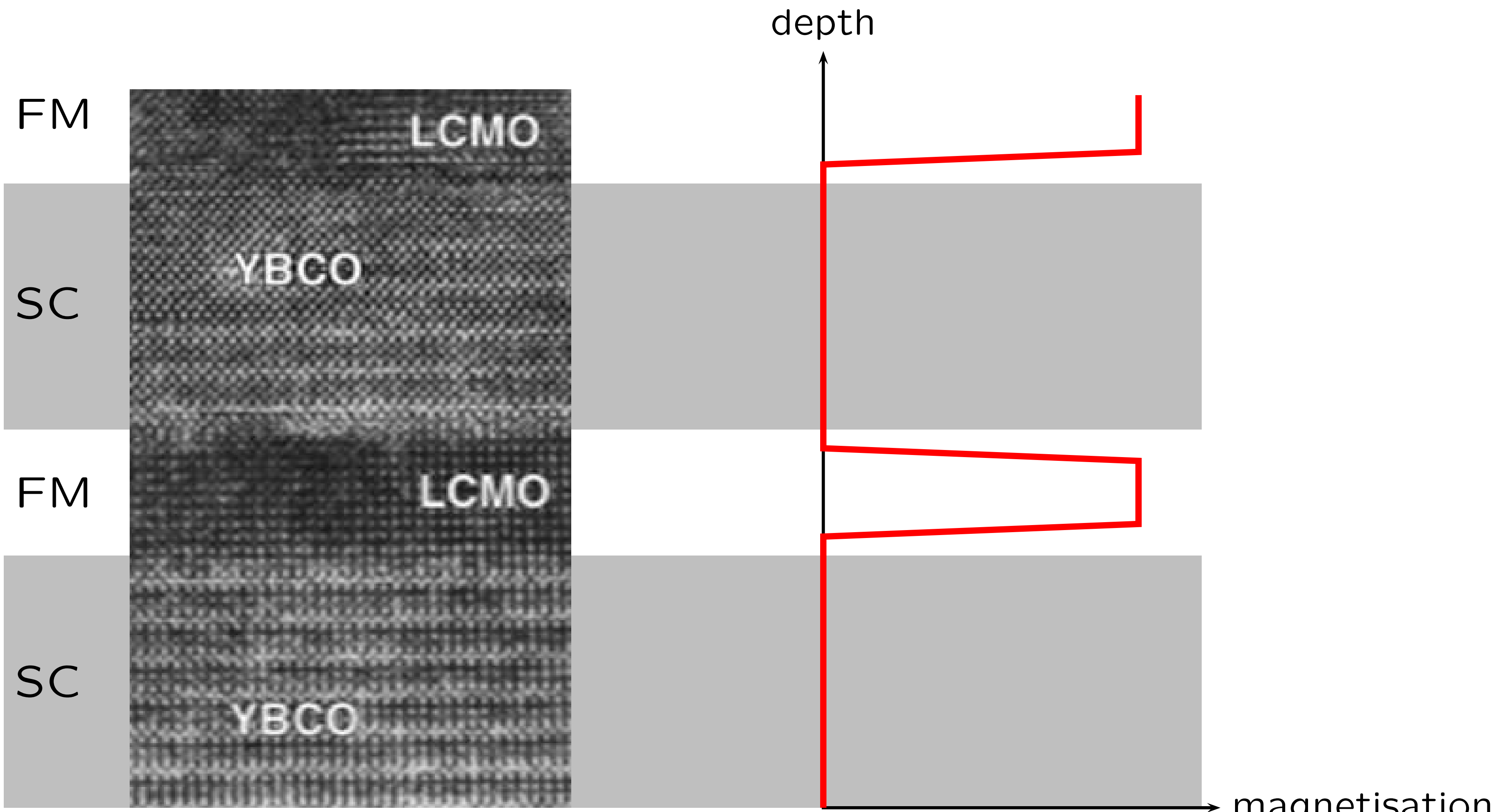
conflict of interests at superconductor / ferromagnet interfaces

(1) no interaction:



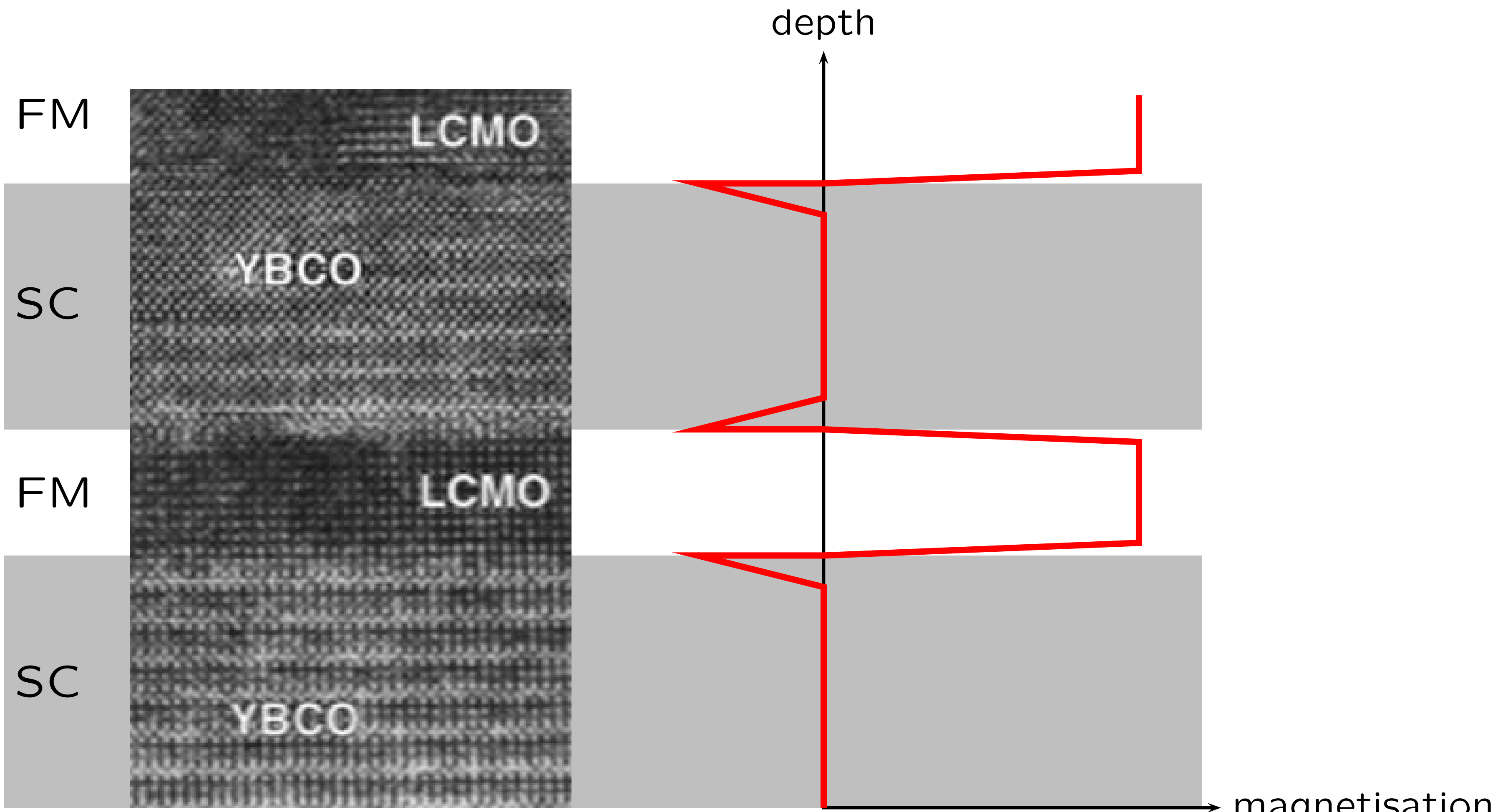
conflict of interests at superconductor / ferromagnet interfaces

(2) suppression of magnetism:



conflict of interests at superconductor / ferromagnet interfaces

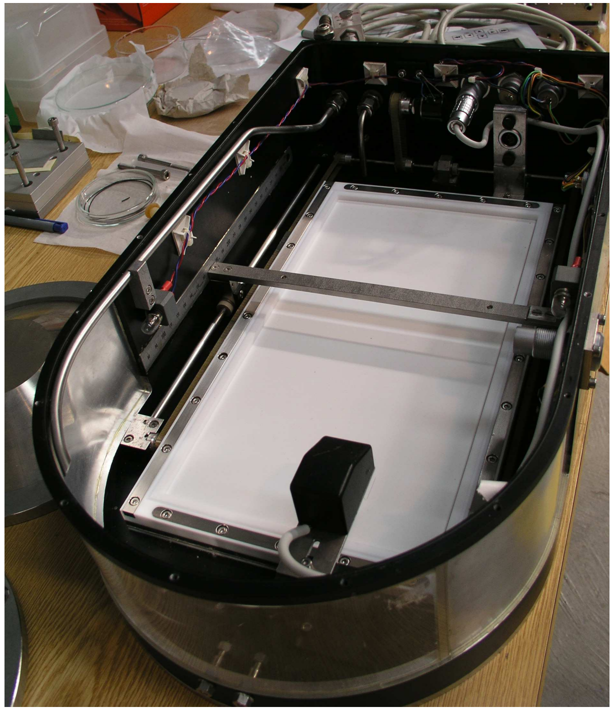
(3) reality: induced magnetism within SC!



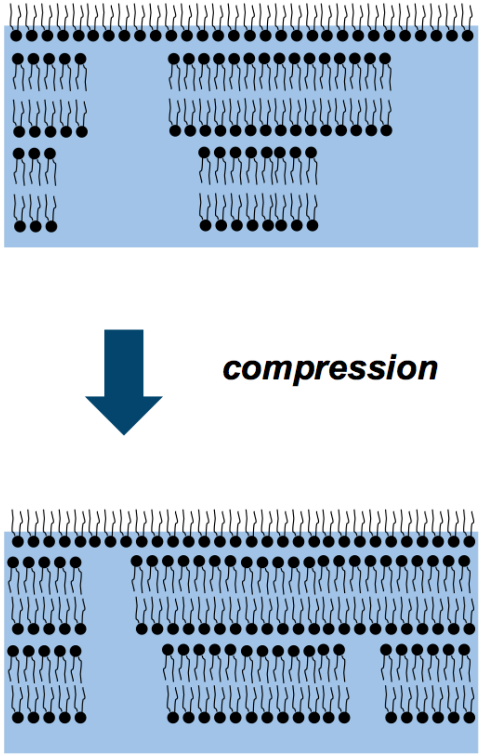
Habermaier, Physica C 364, 298 (2001); Holden, PRB 69, 064505 (2004); Stahn, PRB 71, 140509(R) (2005)

compression of self-organising polyglycerol-ester films

model-system for
foams used for stabilising food products
e.g. yogurt



trough to investigate
membranes at the
liquid/air interface



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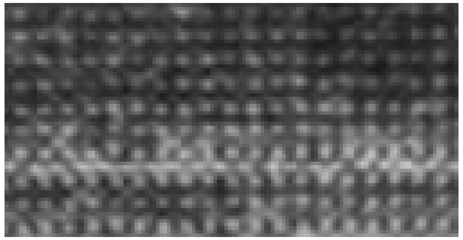
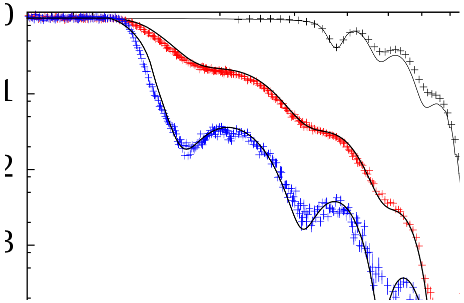
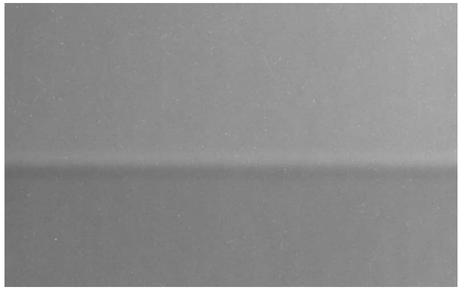


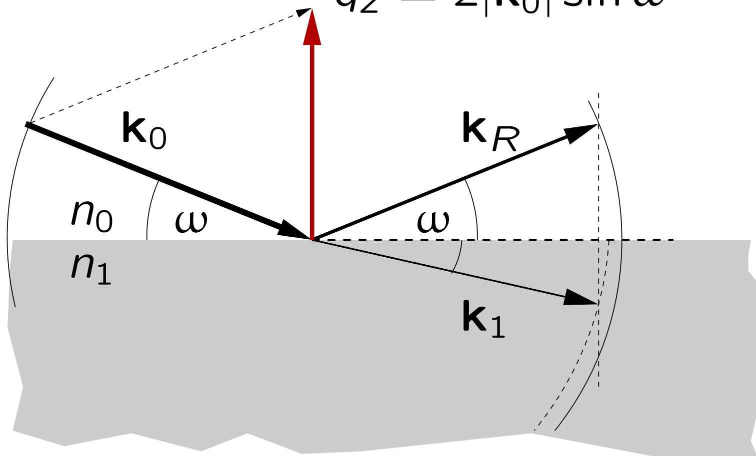
flat surfaces partly reflect light
→ picture of the boot

some media also transmit light
→ ground below the water

parallel interfaces
→ colourful soap bubbles

$q_z = 2|\mathbf{k}_0| \sin\omega$

$|\mathbf{k}| = 2\pi/\lambda$



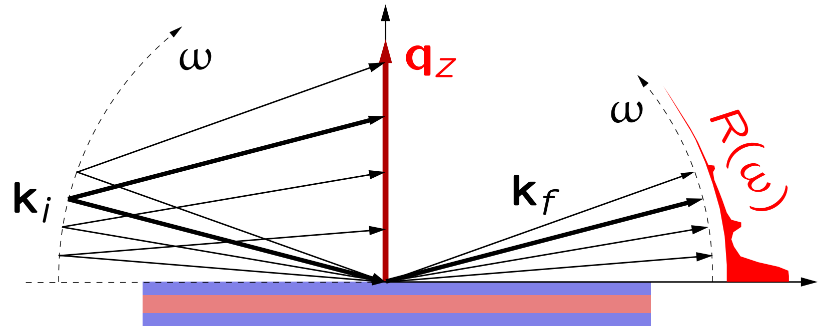
measurement schemes

$$R = R(q_z) = R(\lambda, \omega) \qquad q_z = 4\pi \frac{\sin\omega}{\lambda}$$

angle-dispersive set-up

variation of ω with fixed λ

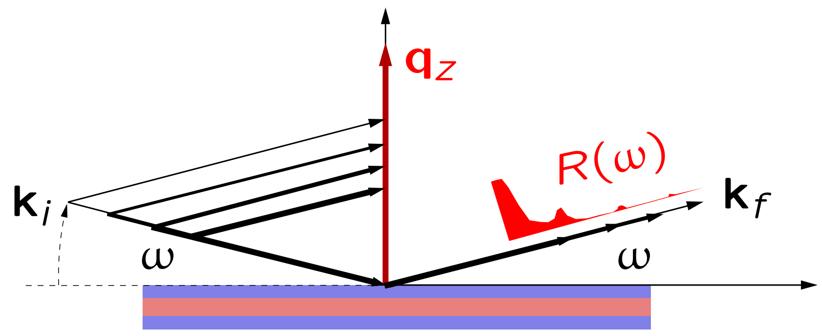
detection under 2ω



energy-dispersive set-up

variation of λ with fixed ω

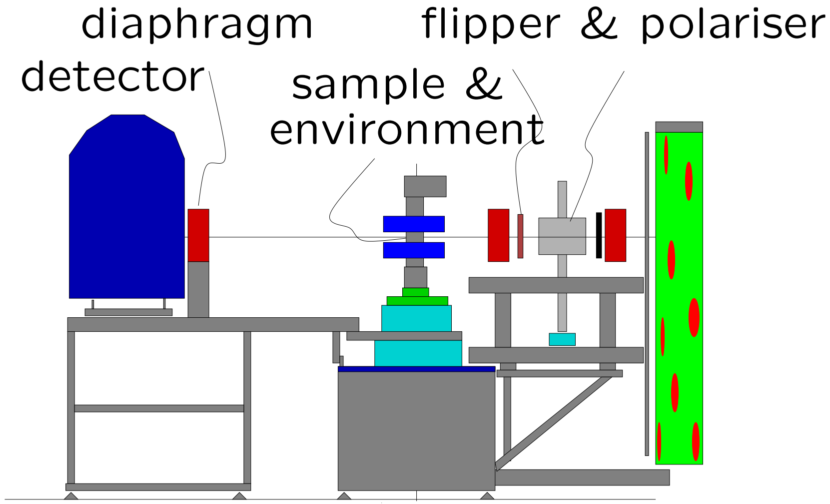
detection via time-of-flight

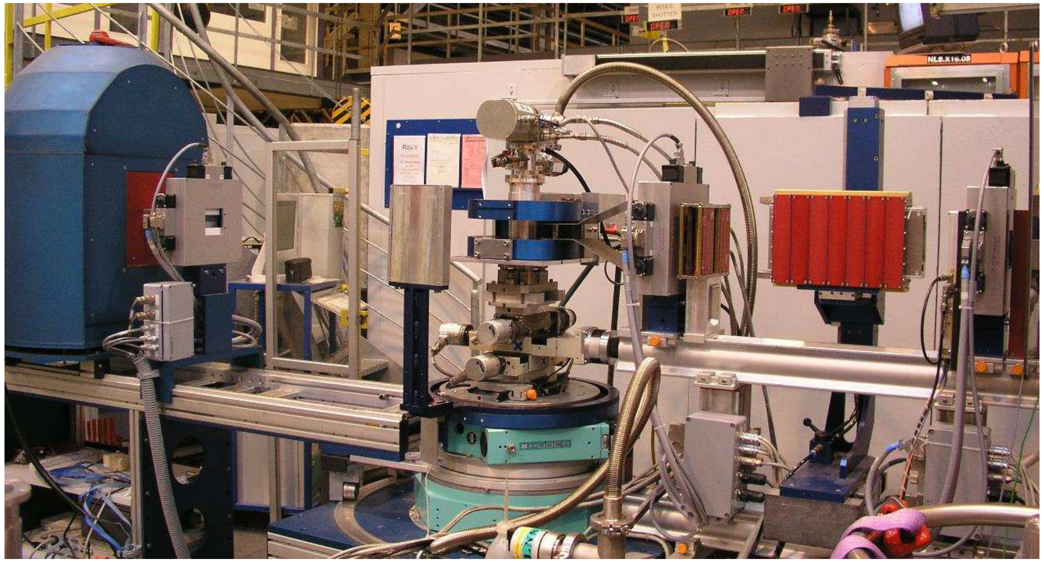


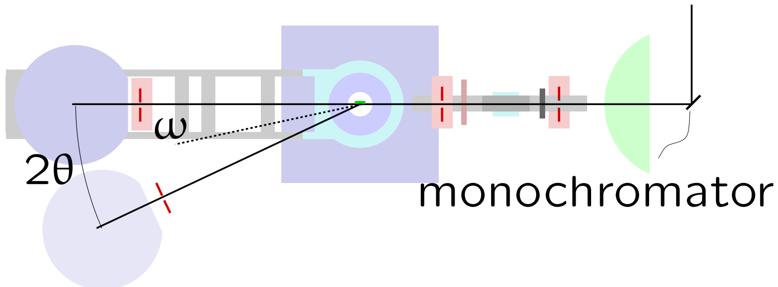
angle-dispersive set-up

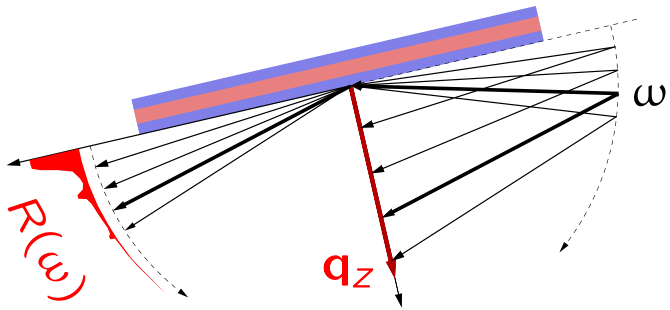
neutron reflectometer

instrument: Morpheus at SINQ





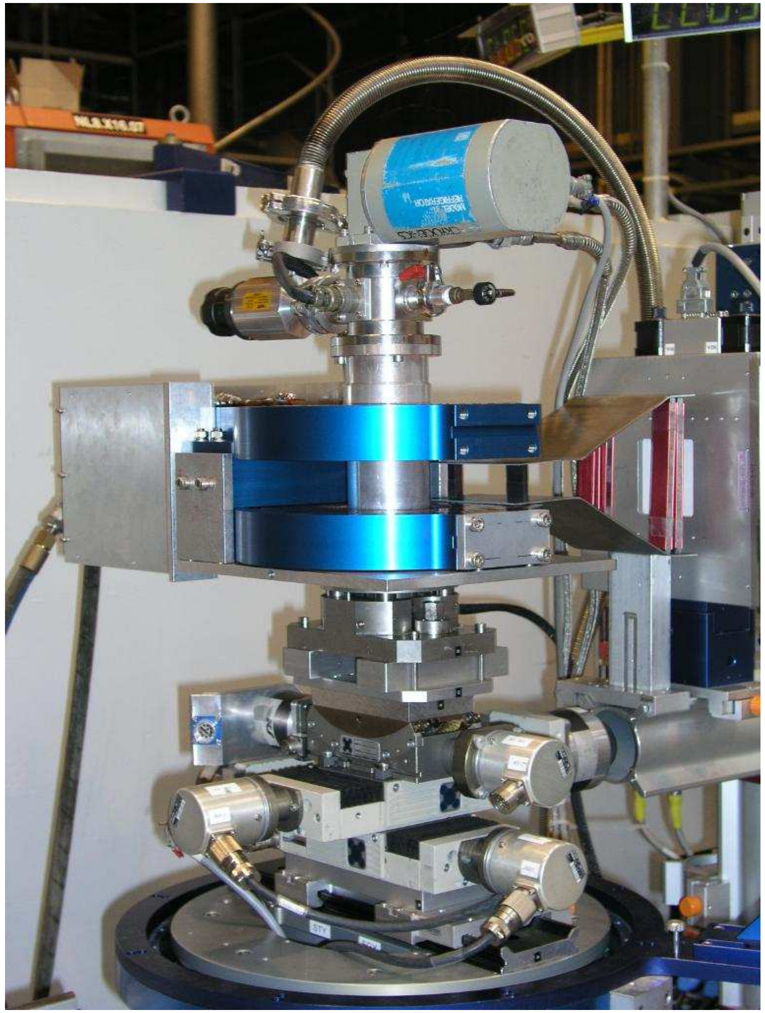




sample environment

cooling with a
closed cycle refrigerator $8\,\mathrm{K} < T < 300\,\mathrm{K}$

application of an external magnetic field with
Helmholtz coils $-1000\,\mathrm{Oe} < H < 1000\,\mathrm{Oe}$

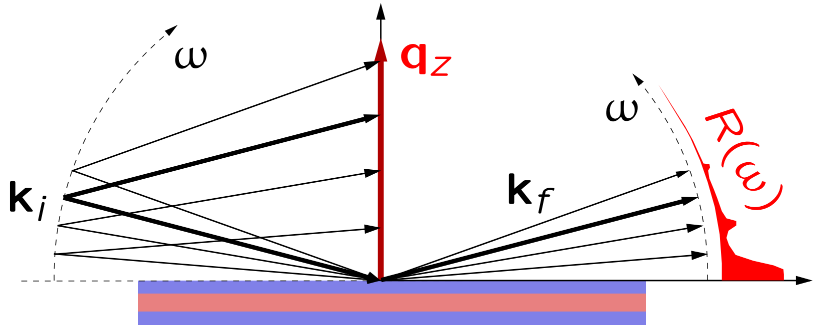


tilt- and
translation stages
for alignment

and **sample**

typical quantities:

angular range	$0^\circ \ldots 10^\circ$
λ range	3 Å … 15 Å
measurement time	10 min … 12h

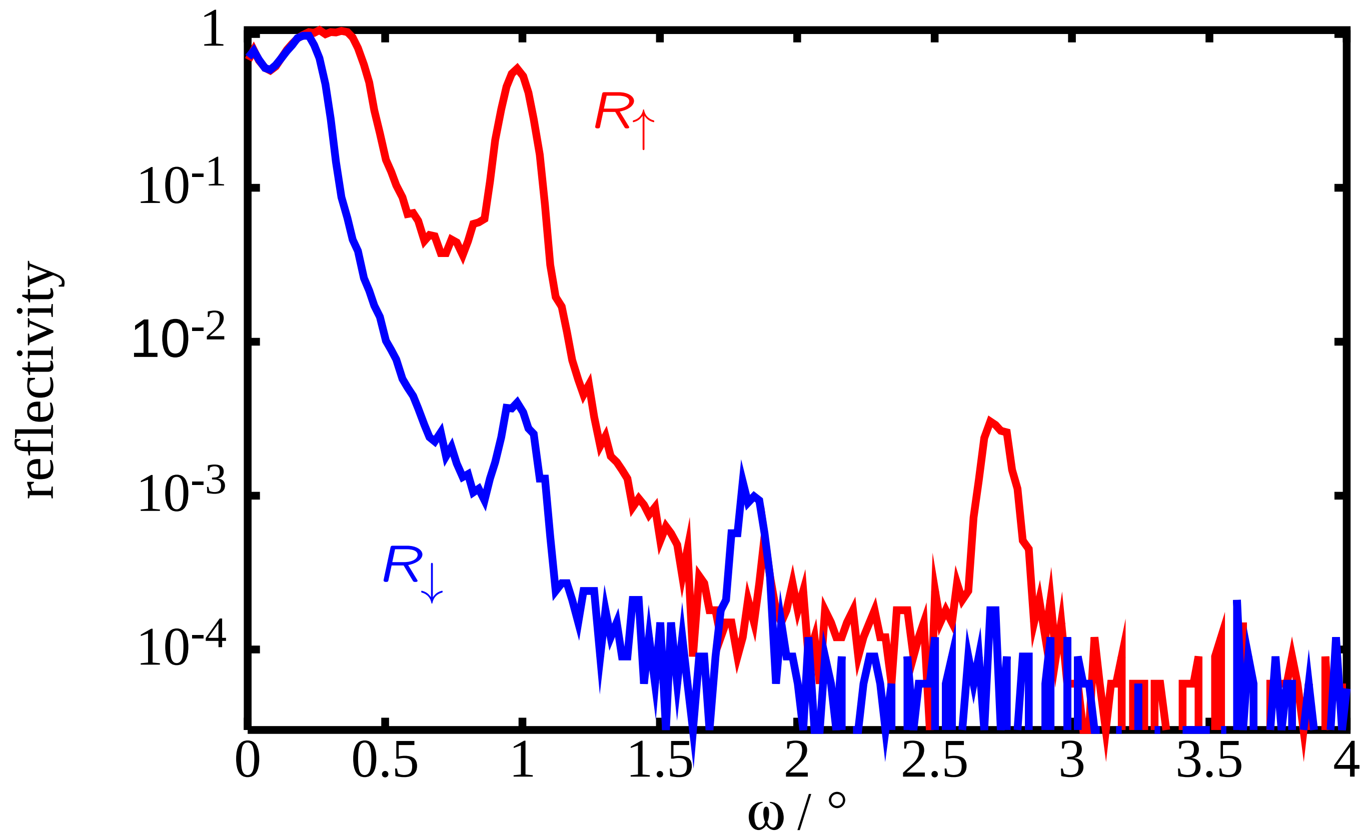


example:

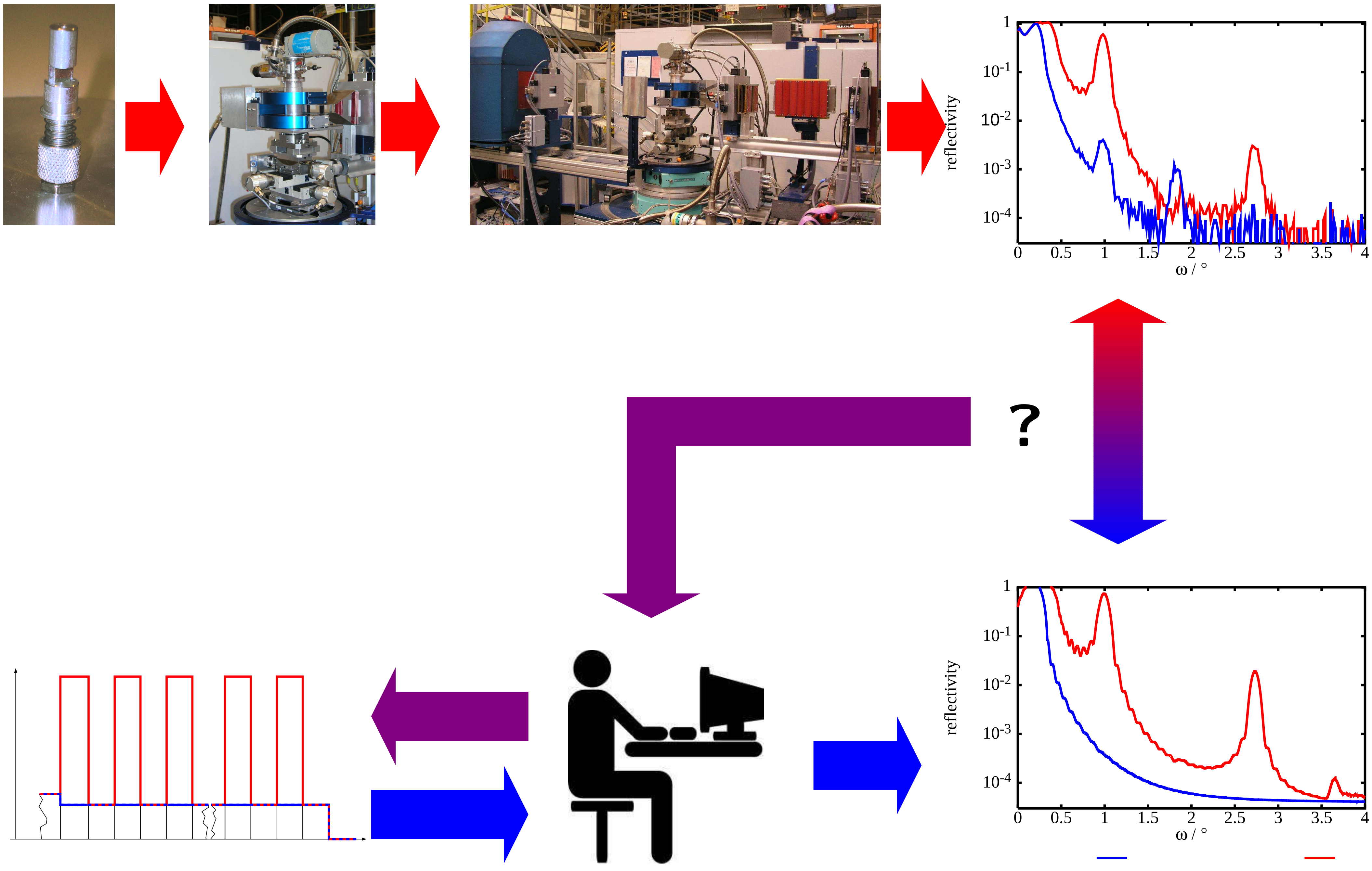
Fe/Si multilayer on glass

polarised neutrons

1h per spin state



from the sample to $\rho(z)$



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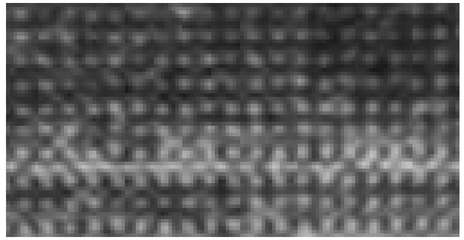

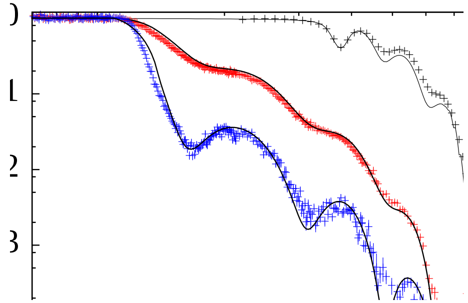

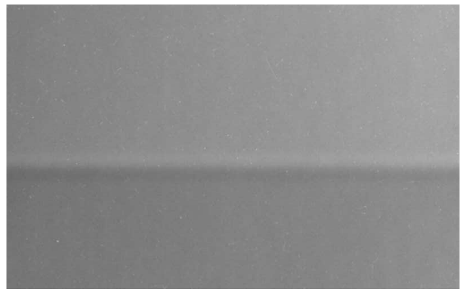

flat surfaces partly reflect light
→ picture of the boot

some media also transmit light
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parallel interfaces
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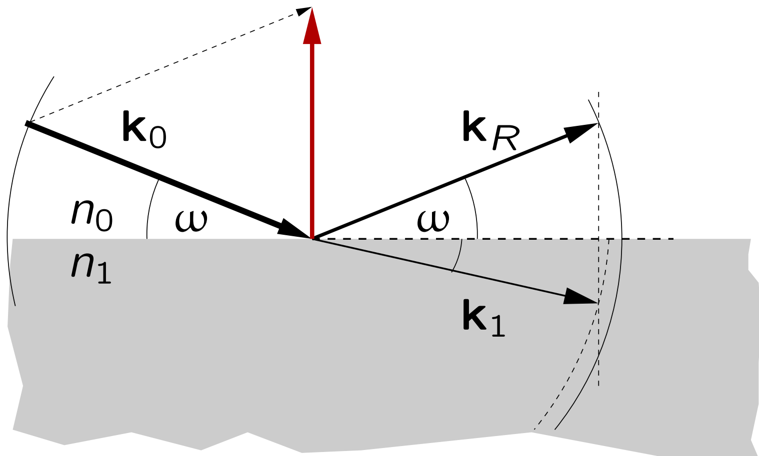
scientist's explanation:

- index of refraction,
- Fresnel reflectivity,
- transmittance,
- interference,
- bla bla bla . . .

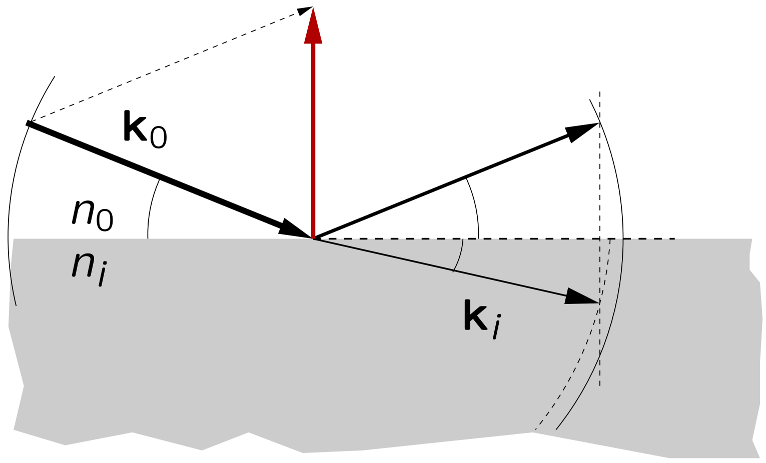


plane wave in a medium i:

$$\frac{\hbar^2}{2m}\frac{\mathrm{d}^2}{\mathrm{d}r^2} A\,\mathrm{e}^{\mathrm{i}k_i r} \;+\; (E - V_i)\,A\,\mathrm{e}^{\mathrm{i}k_i r} \;=\; 0$$

$$\frac{\hbar^2}{2m}(-k_i^2)\mathrm{e}^{\mathrm{i}k_i r} \;+\; (E - V_i)\,\mathrm{e}^{\mathrm{i}k_i r} \;=\; 0$$

$$\Rightarrow k_i^2 \;=\; (E - V_i)\,\frac{2m}{\hbar^2}$$



$$n_i^2 \;=\; \frac{k_i^2}{k_0^2} \qquad \text{by definition}$$

$$\;=\; \frac{E - V_i}{E} \qquad \text{with } V_0 = 0 \text{ (vacuum)}$$

$$n_i \;=\; \sqrt{1 - V_i/E}$$

$$\;\approx\; 1 - V_i/2E \qquad \text{for } V_i \ll E$$

$$\;:=\; 1 - \delta \qquad n_i - 1 \propto V_i \quad \Rightarrow \quad \textbf{what is } V_i\textbf{?}$$

what is V_i for x-rays?

interaction γ / electron

(off-resonance)

$$V^{\mathrm{e}} = \frac{2\pi\hbar^2}{m_{\mathrm{e}}} \frac{r_{\mathrm{e}}}{\mathrm{vol}} \sum_i Z_i = \frac{2\pi\hbar^2}{m_{\mathrm{e}}} r_{\mathrm{e}} \, \rho^{\mathrm{e}}$$

with

Z_i = electron number of atom i

r_{e} = electron radius

m_{e} = electron mass

$$\delta = \frac{\lambda^2}{2\pi} r_{\mathrm{e}} \, \rho^{\mathrm{e}}$$

with absorption: complex n

$$n = 1 - \delta - \mathrm{i}\beta$$

at resonances:

$$\delta = \delta(\mathbf{B})$$

what is V_i for neutrons?

interaction neutron / nucleus j

with $\lambda \gg r_{\mathrm{nucleus}\,j}$

$$\begin{aligned} V_j^{\mathrm{Fermi}} &= b_j \frac{2\pi\hbar^2}{m_\mathrm{n}} \delta(\mathbf{r}) \\ V^\mathrm{n} &= \frac{1}{\mathrm{vol}} \int_j V_j^{\mathrm{Fermi}} \, \mathrm{d}\mathbf{r} \\ &= \frac{2\pi\hbar^2}{m_\mathrm{n}} \frac{1}{\mathrm{vol}} \sum_j b_j \\ &:= \frac{2\pi\hbar^2}{m_\mathrm{n}} \rho^b \end{aligned}$$

interaction neutron magnetic moment $\boldsymbol{\mu}$ / magnetic induction $\mathbf{B}$

$$\begin{aligned} \boldsymbol{\mu} \uparrow\uparrow \mathbf{B} &\Rightarrow V^\mathrm{m} = +\mu B \\ \boldsymbol{\mu} \uparrow\downarrow \mathbf{B} &\Rightarrow V^\mathrm{m} = -\mu B \\ \boldsymbol{\mu} \perp \mathbf{B} &\Rightarrow \text{ spin-flip scattering} \end{aligned}$$

$$\begin{aligned} V^\mathrm{m} &= \boldsymbol{\mu}\, \mathbf{B}_\perp \\ &:= \frac{2\pi\hbar^2}{m_\mathrm{n}} \rho^\mathrm{m} \end{aligned}$$

$$m_\mathrm{n} = \text{neutron mass}$$

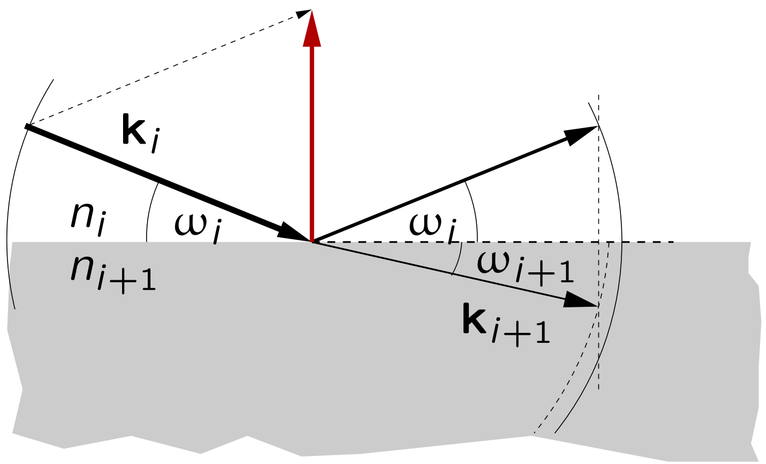
what is the reflected intensity?

assumptions:

– one interface, only

– ideally flat and sharp

– homogeneous in x and y
$\Rightarrow$ only normal (z) components are relevant



continuity conditions for a plane wave impinging on the interface $i, i+1$:

$$\begin{aligned}\Psi_{z,i} &= \Psi_{z,i+1}\\ \frac{\mathrm{d}}{\mathrm{d}z}\Psi_{z,i} &= \frac{\mathrm{d}}{\mathrm{d}z}\Psi_{z,i+1}\end{aligned}$$

with

$$\begin{aligned}\Psi_{z,j} &= A_j^{\uparrow}\mathrm{e}^{\mathrm{i}k_{z,j}z} + A_j^{\downarrow}\mathrm{e}^{-\mathrm{i}k_{z,j}z}\\ k_{z,j} &= k_j \sin\omega_j\\ &= n_j k_0 \sin\omega_j\end{aligned}$$

reflectance

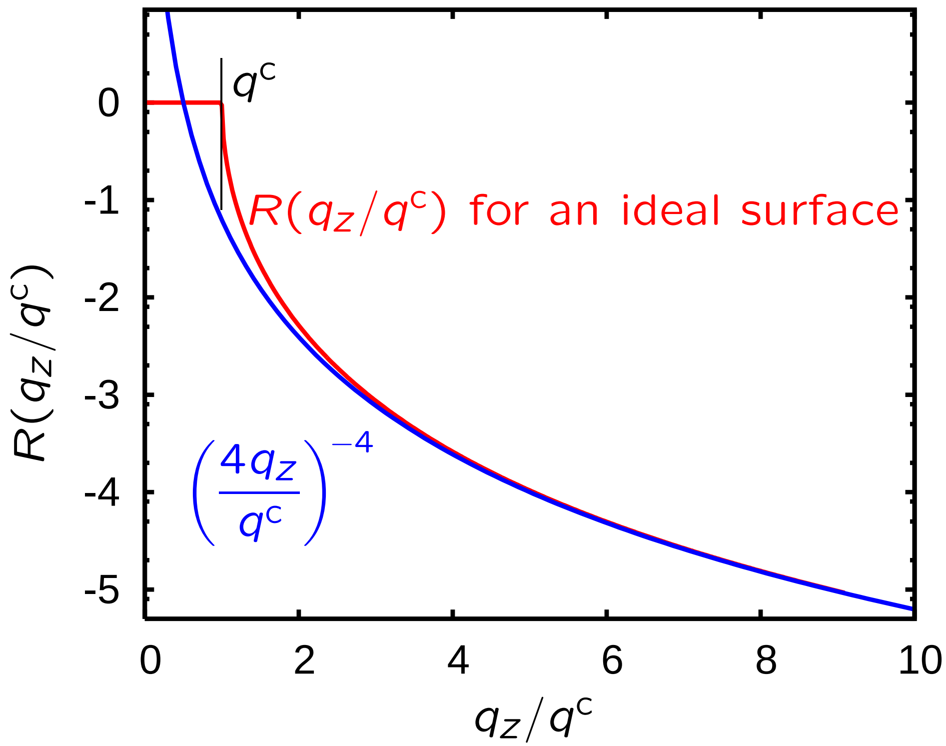
$$\begin{aligned}r_{i,i+1} &= \frac{A_i^{\uparrow}}{A_i^{\downarrow}}\\ &\vdots\\ &= \frac{n_i \sin\omega_i - n_{i+1}\sin\omega_{i+1}}{n_i \sin\omega_i + n_{i+1}\sin\omega_{i+1}}\end{aligned}$$

reflectance — for $\omega_{i+1} > 0$

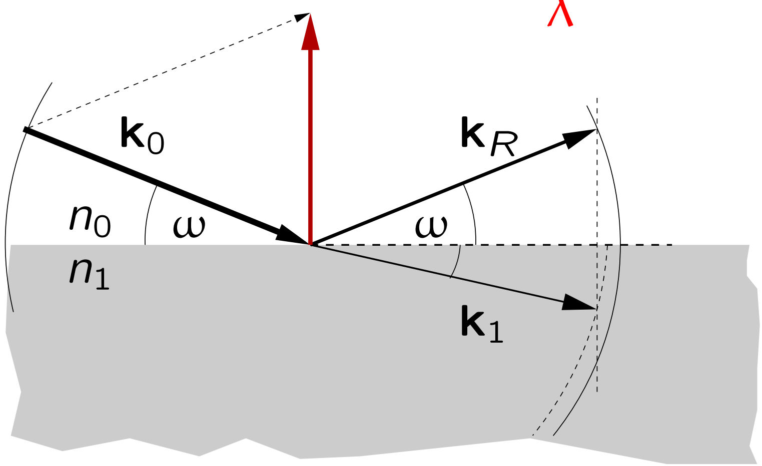
$$r_{i,i+1} = \frac{n_i \sin\omega_i - n_{i+1} \sin\omega_{i+1}}{n_i \sin\omega_i + n_{i+1} \sin\omega_{i+1}}$$

transmittance — for $\omega_{i+1} > 0$

$$t_{i,i+1} = \frac{2\, n_i \sin\omega_i}{n_i \sin\omega_i + n_{i+1} \sin\omega_{i+1}}$$



$$q_z = 2 \cdot \frac{2\pi}{\lambda} \cdot \sin\omega$$



air/solid interface — for $q_z > q^c$

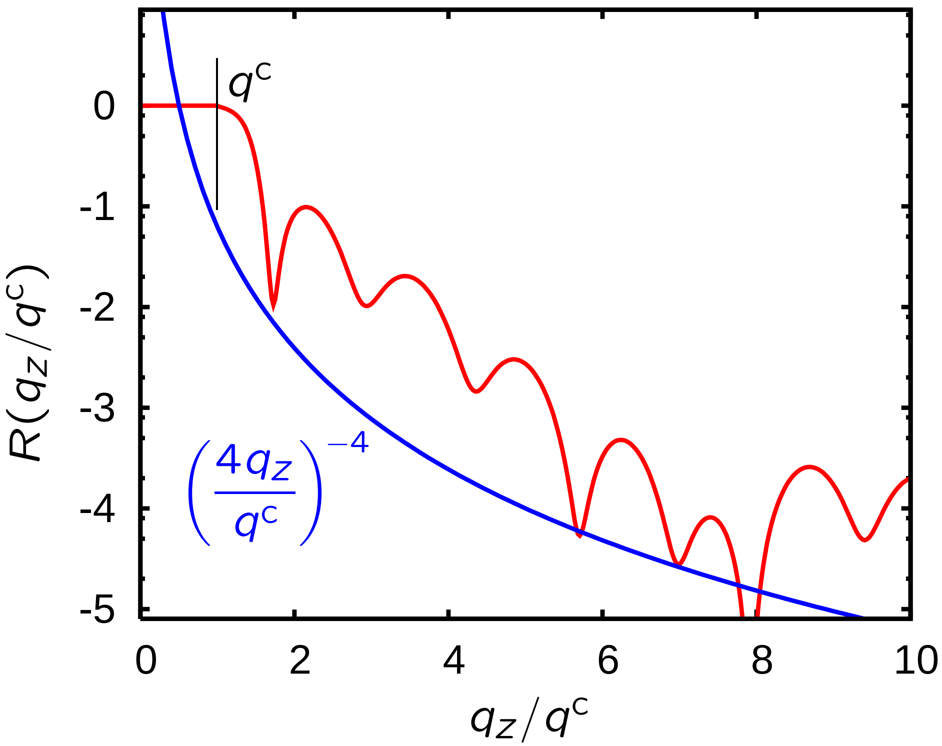
$$r_{0,1} = \frac{1 - \sqrt{1 - (q^c/q_z)^2}}{1 + \sqrt{1 - (q^c/q_z)^2}}$$

$$R(q_z) = |r_{0,1}(q_z)|^2$$

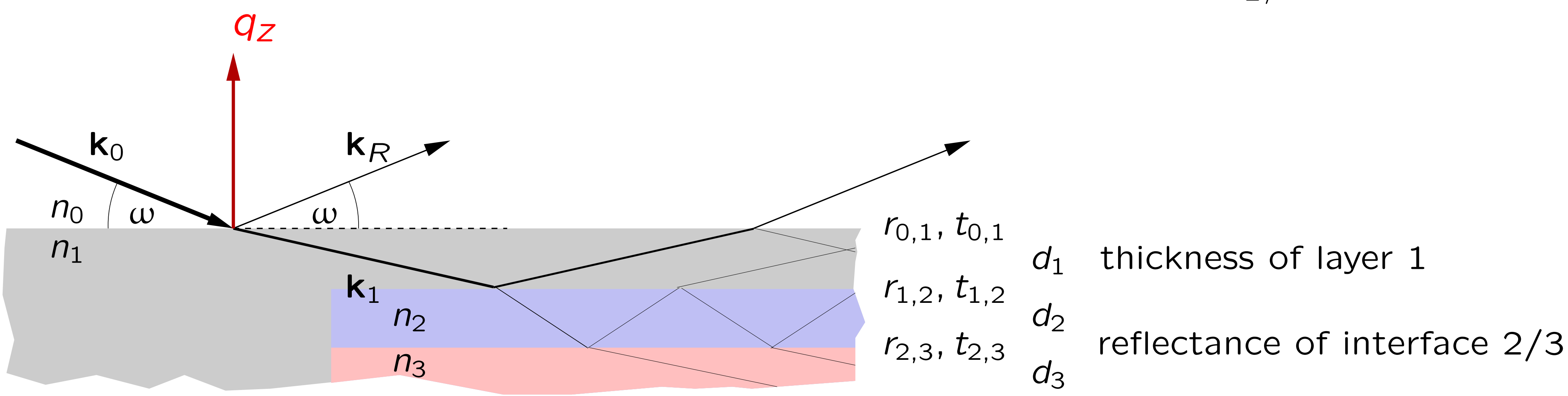
several parallel interfaces:

interference of all waves

$$R(q_z) \;=\; \left|r(q_z)\right|^2$$



what is $r(q_z)$ of a multilayer?



what is $r(q_z)$ of a multilayer?

$$\Psi_0(0) = \begin{pmatrix} A_0^{\uparrow} \\ A_0^{\downarrow} \end{pmatrix}$$

free choice of phase

$$= \begin{pmatrix} 1/t_{0,1} & r_{0,1}/t_{0,1} \\ r_{0,1}/t_{0,1} & 1/t_{0,1} \end{pmatrix} \begin{pmatrix} A_1^{\uparrow} \\ A_1^{\downarrow} \end{pmatrix}$$

continuity condition

$$= \mathbf{I}_{0,1} \begin{pmatrix} e^{ik_{z,1}d_1} & 0 \\ 0 & e^{-ik_{z,1}d_1} \end{pmatrix} \begin{pmatrix} A_1^{\uparrow}\, e^{-ik_{z,1}d_1} \\ A_1^{\downarrow}\, e^{ik_{z,1}d_1} \end{pmatrix}$$

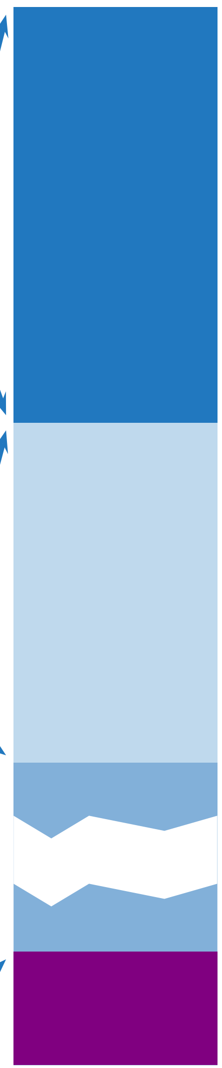
phase factor

$$= \mathbf{I}_{0,1}\mathbf{T}_1 \begin{pmatrix} 1/t_{1,2} & r_{1,2}/t_{1,2} \\ r_{1,2}/t_{1,2} & 1/t_{1,2} \end{pmatrix} \begin{pmatrix} A_2^{\uparrow}\, e^{-ik_{z,1}d_1} \\ A_2^{\downarrow}\, e^{ik_{z,1}d_1} \end{pmatrix}$$

$$= \mathbf{I}_{0,1}\mathbf{T}_1\mathbf{I}_{1,2} \begin{pmatrix} e^{ik_{z,2}d_2} & 0 \\ 0 & e^{-ik_{z,2}d_2} \end{pmatrix} \begin{pmatrix} A_2^{\uparrow}\, e^{-ik_{z,2}(d_1+d_2)} \\ A_2^{\downarrow}\, e^{ik_{z,2}(d_1+d_2)} \end{pmatrix}$$

$$\vdots$$

$$:= \mathbf{M} \begin{pmatrix} A_{\text{substr}}^{\uparrow}\, e^{-ik_{z,\text{substr}}\sum_i d_i} \\ A_{\text{substr}}^{\downarrow}\, e^{ik_{z,\text{substr}}\sum_i d_i} \end{pmatrix}$$



what is $r(q_z)$ of a multilayer?

$$\Psi_0(0) = \begin{pmatrix} A_0^{\uparrow} \\ A_0^{\downarrow} \end{pmatrix}$$

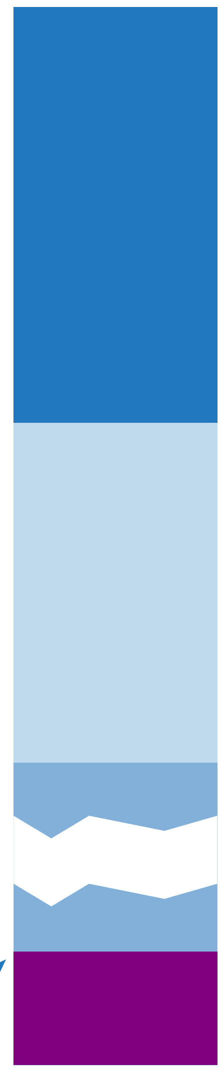
$$= \mathbf{M} \begin{pmatrix} 0 \\ A_{\text{substr}}^{\downarrow}\, e^{i k_{z,\text{substr}} \sum_i d_i} \end{pmatrix}$$

$$r(q_z) = A_0^{\uparrow} / A_0^{\downarrow}$$

$$= \frac{M_{1\,2}\, A_{\text{substr}}^{\downarrow}\, e^{i k_{z,\text{substr}} \sum_i d_i}}{M_{2\,2}\, A_{\text{substr}}^{\downarrow}\, e^{i k_{z,\text{substr}} \sum_i d_i}}$$

$$= \frac{M_{1\,2}(q_z)}{M_{2\,2}(q_z)}$$

there is no upcoming wave



calculation of $M_{1\,2}(q_z)$ and $M_{2\,2}(q_z)$ is trivial . . .

. . . if all n_i and d_i are known!

reflected intensity of a multilayer

$$R(q_z) = |r(q_z)|^2$$

$\Rightarrow$ all phase information is lost

$\Rightarrow$ one way road:

$\Rightarrow$ calculation of $R(q_z)$ using a model
and
comparison to measured curve(s)

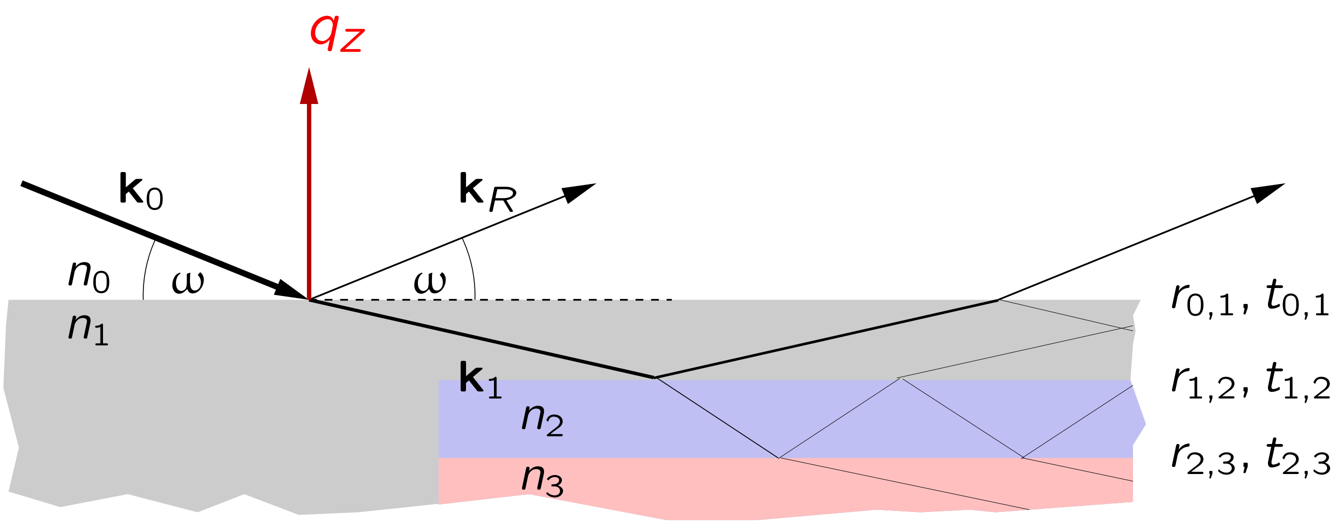
real effects
to be taken into account:

– non-sharp interfaces

– inhomogeneous layers

– illumination of the sample

– resolution of the set-up
$\Delta\omega$, $\Delta\lambda$

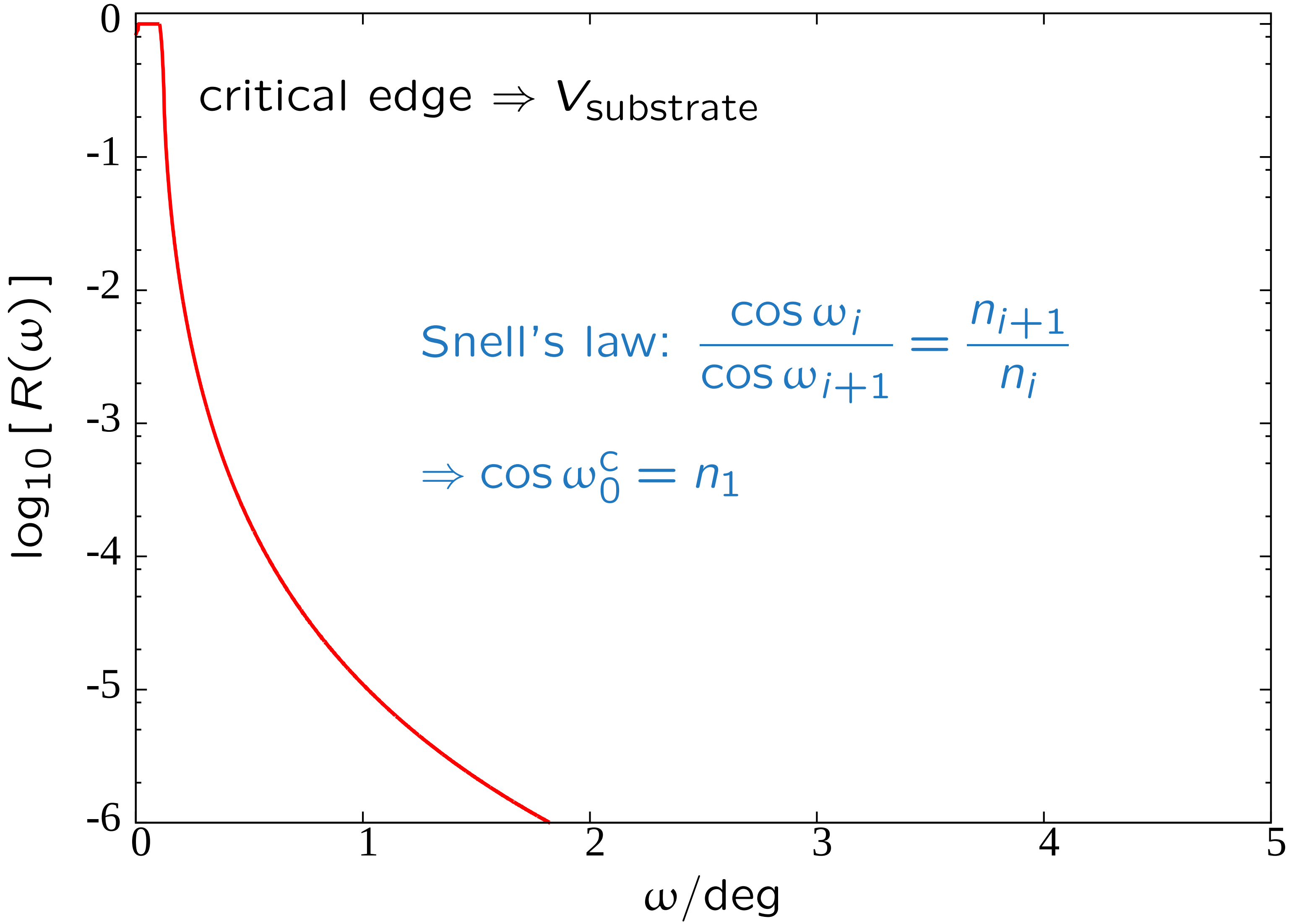


d_1 thickness of layer 1

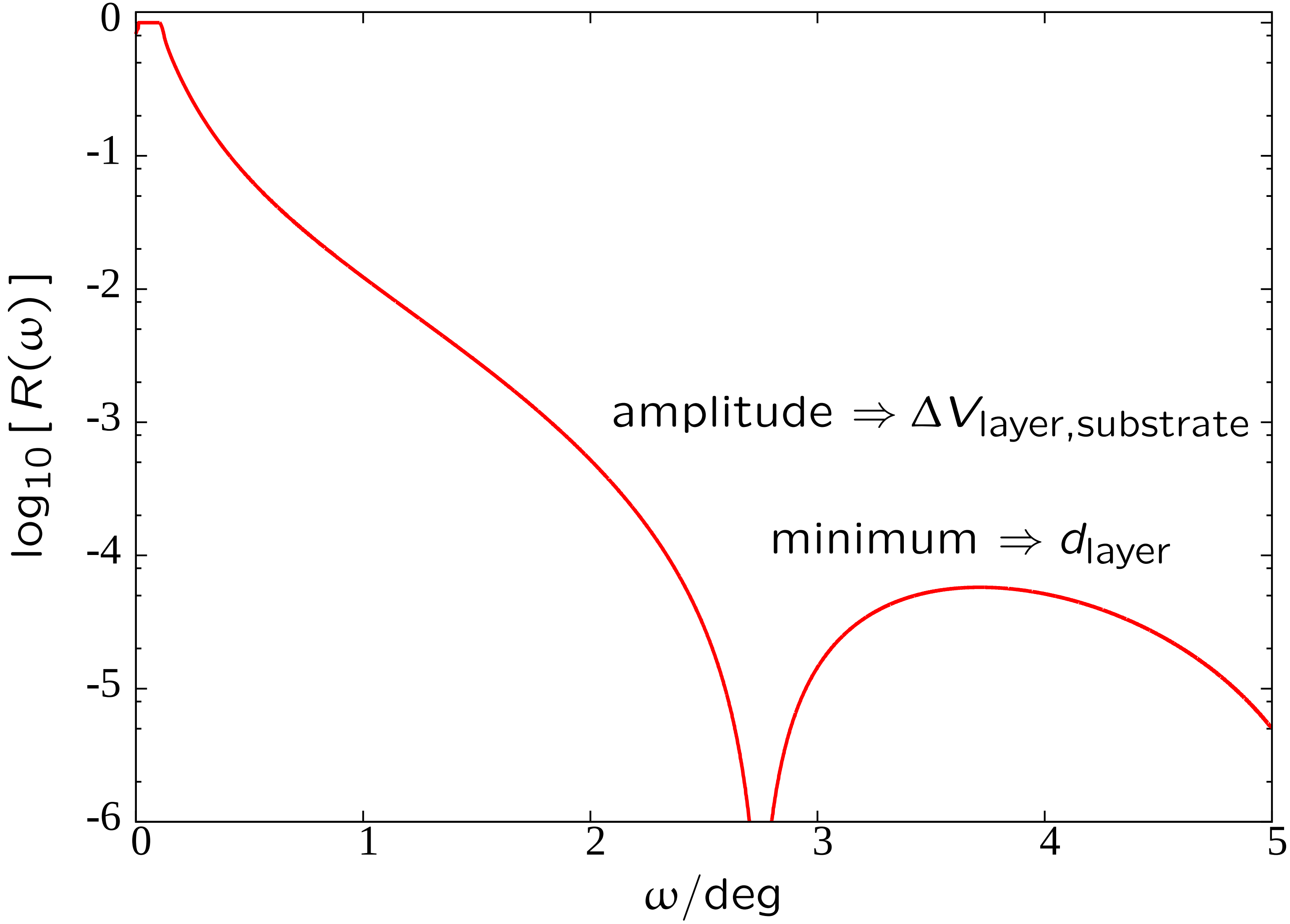
d_2 reflectance of interface 2/3

d_3

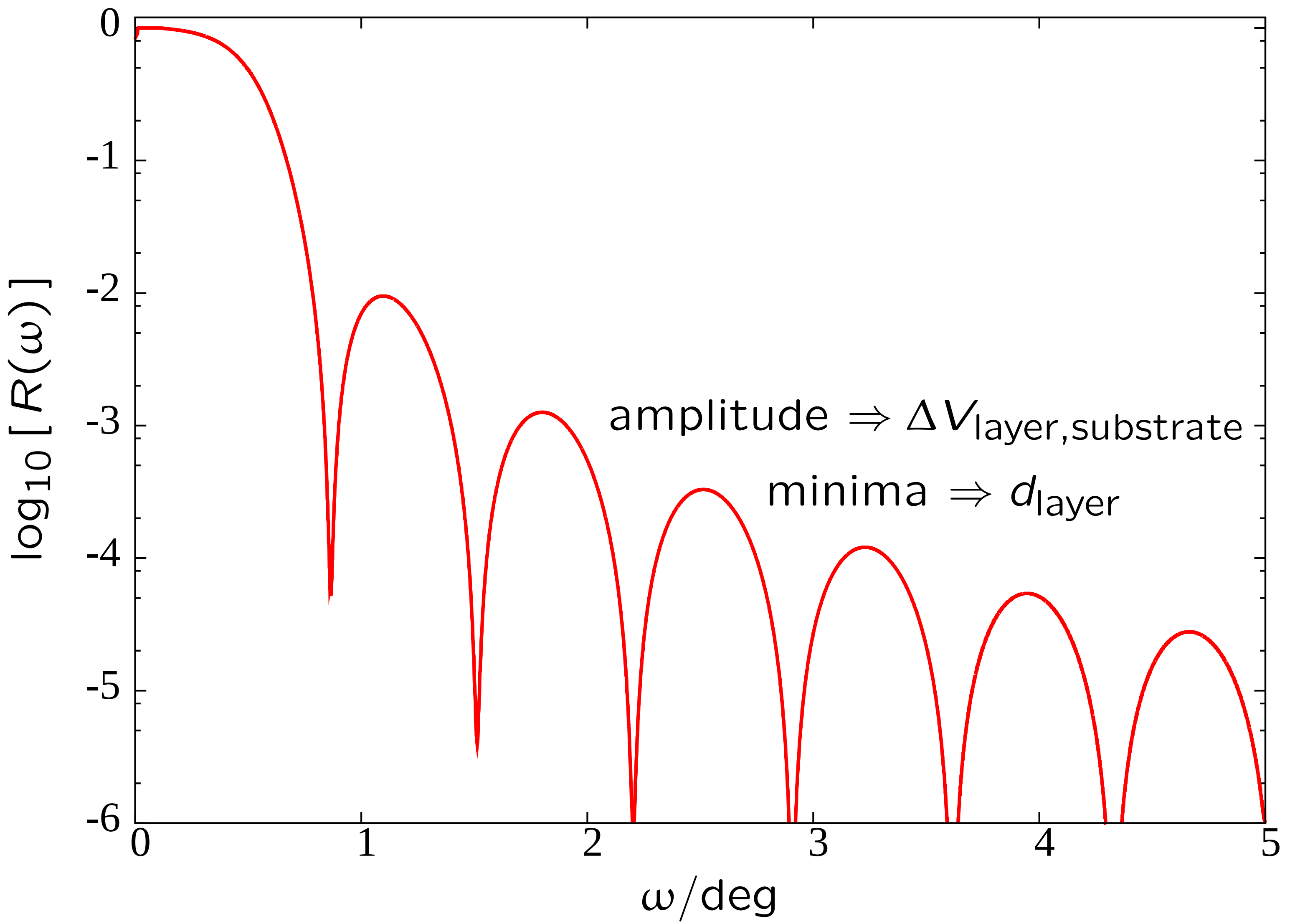
. . . of a surface

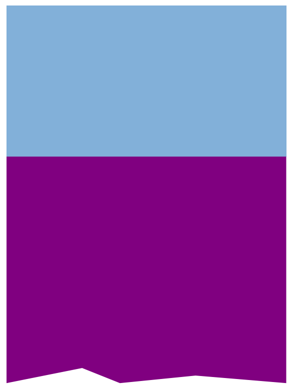

critical edge ⇒ $V_{\text{substrate}}$
Snell's law: $\dfrac{\cos\omega_i}{\cos\omega_{i+1}} = \dfrac{n_{i+1}}{n_i}$
$\Rightarrow \cos\omega_0^c = n_1$
$\log_{10}[R(\omega)]$
ω/deg
0
-1
-2
-3
-4
-5
-6
0
1
2
3
4
5

... of a thin layer

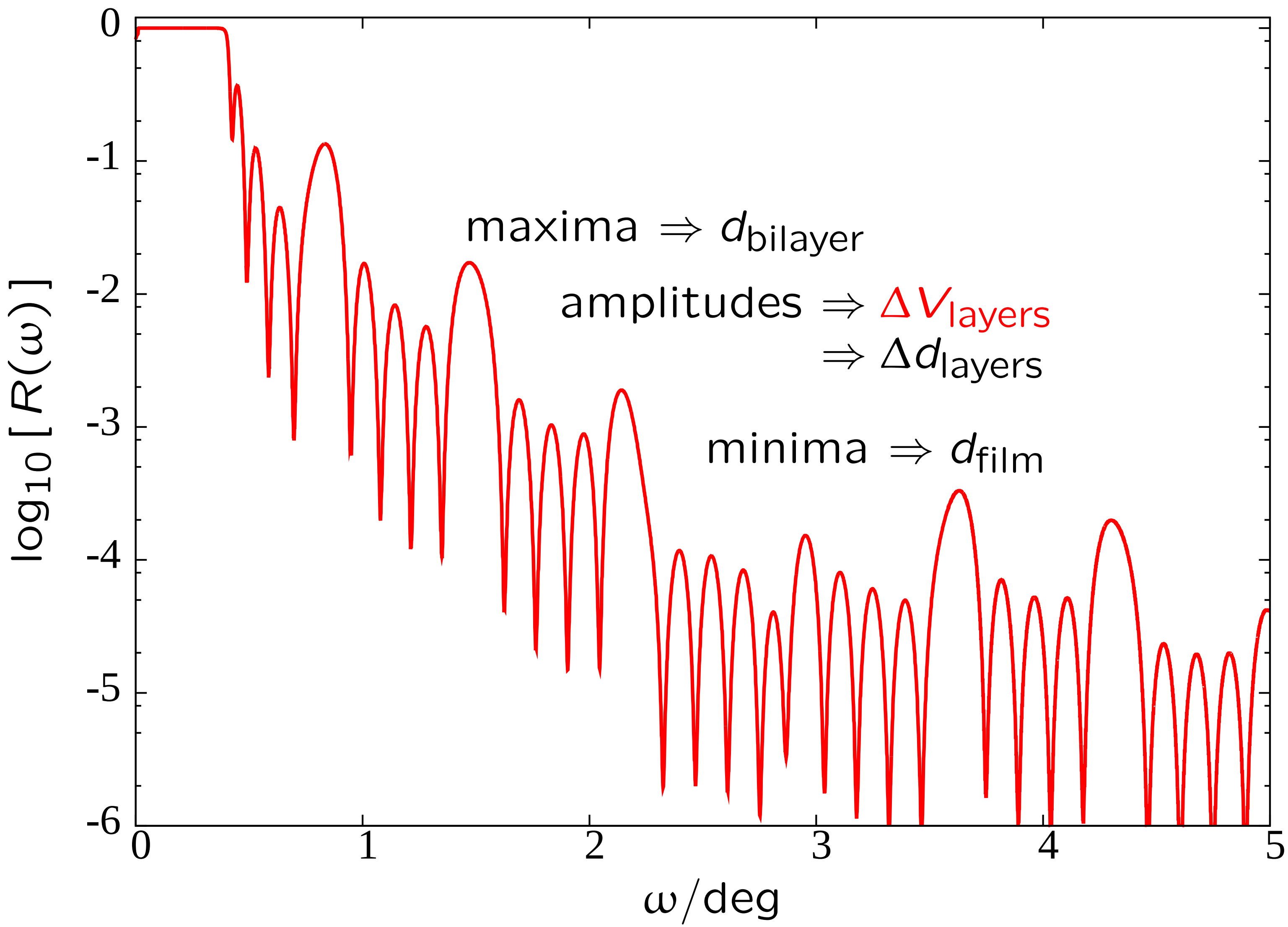


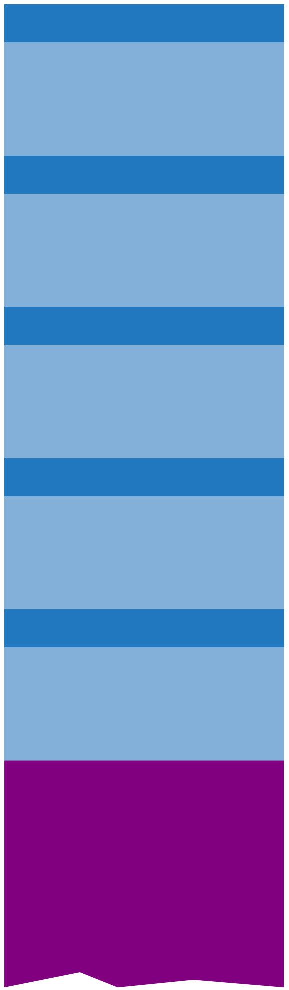
. . . of a thick layer





...of a periodic multilayer





some numbers

$$\delta = 1 - n = \frac{\lambda^2}{2\pi}(\rho^b + \rho^{\mathrm{m}}) \text{ for neutrons}$$
$$= \frac{\lambda^2}{2\pi} r_{\mathrm{e}}\, \rho^{\mathrm{e}} \text{ for x-rays}$$

Ni: $\rho^b = 9.4 \cdot 10^{-6}\,\text{Å}^{-2}$

$\Rightarrow \delta^{\mathrm{nuc}} = 3.75 \cdot 10^{-5}\,, \lambda = 5\,\text{Å}$ $\delta \ll 1$

$\Rightarrow \omega^{\mathrm{c}} \approx 0.5^\circ$ small angles of incidence!

Fe: $\rho^{\mathrm{m}} \approx 6 \cdot 10^{-6}\,\text{Å}^{-2}$

$\Rightarrow \delta^{\mathrm{m}} \approx 2.4 \cdot 10^{-5}\,, \lambda = 5\,\text{Å}$ $\delta^{\mathrm{m}} \sim \delta^b$

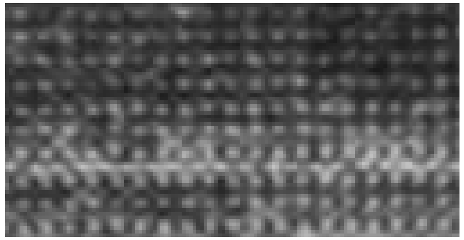
Al: $r_{\mathrm{e}}\, \rho^{\mathrm{e}} = 2.2 \cdot 10^{-5}\,\text{Å}^{-2}$

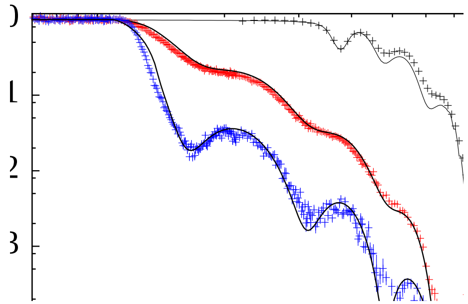
$\Rightarrow \delta^{\mathrm{e}} = 8.7 \cdot 10^{-5}\,, \lambda = 5\,\text{Å}$ $\delta^{\mathrm{e}} \sim \delta^b$

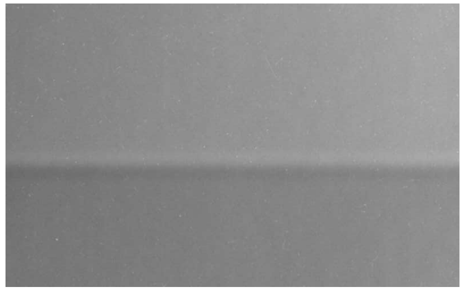
probed depth	$100\,\mathrm{nm} \to 1\,\mu\mathrm{m}$	(less for strong absorbers)
depth resolution	$0.2\,\mathrm{nm} \to 400\,\mathrm{nm}$	strongly model dependent t and δ might be strongly correlated
lateral coherence	$1\,\mu\mathrm{m} \to 100\,\mu\mathrm{m}$	averaging laterally over all *microstructures*

outline

- heterostructures
  - → magnetic layers
  - → membrane systems
- reflectometry
  - → (few formulae)
- . . . derivation
  - → (lots of formulae)
- **experimental examples**
  - → Fe/Si
  - → FeSi/GaAs interfaces
  - → bio-membrane
- relevance for imaging
  - → YES, there is some!

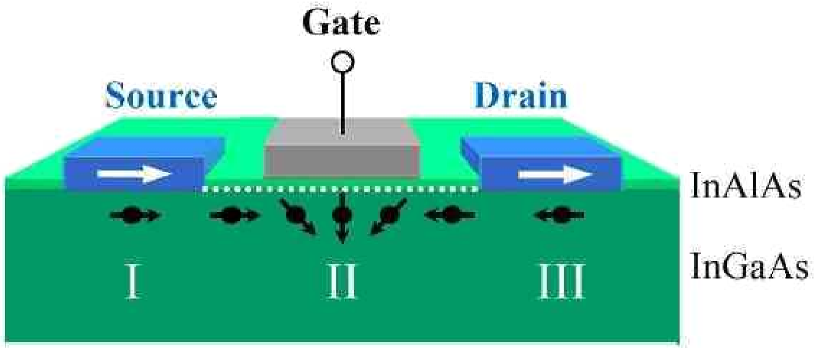






use not only the electron charge to carry information but also its spin

e.g. transistor based on spin / FM alignment:



spin-polarised currents exist in *half-metals* (e.g. Fe_3Si)

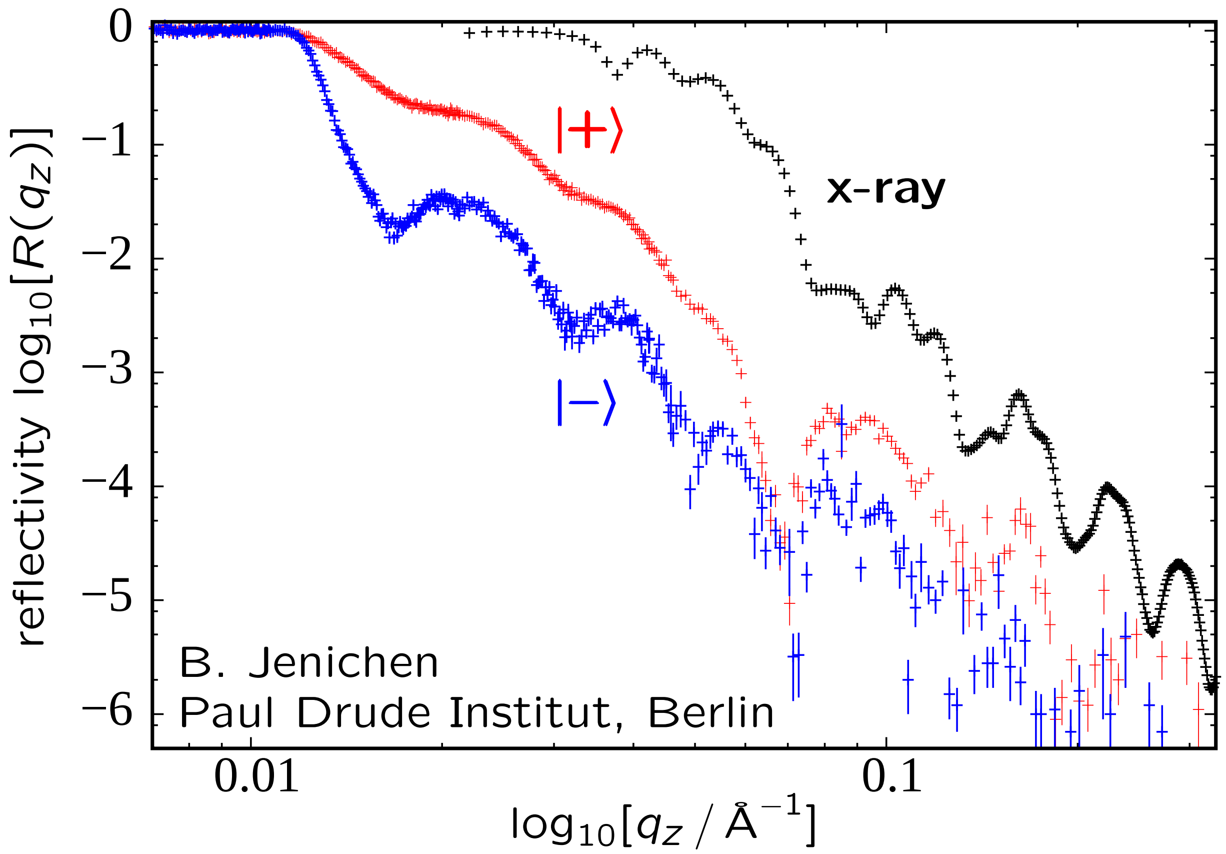
but

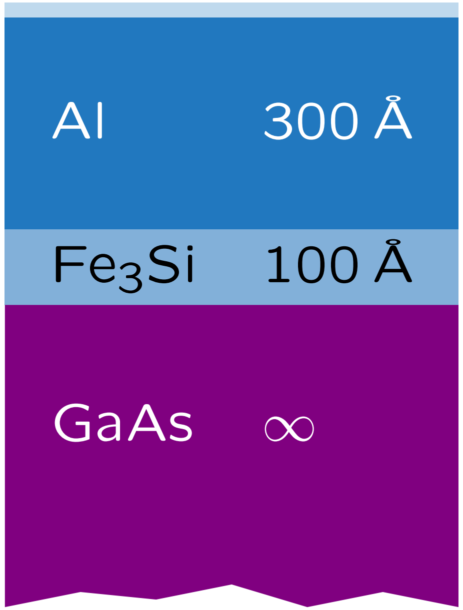
polarised spin injection into a semiconductor (e.g. GaAs) is inefficient

$\Rightarrow$ what happens at the interface?

Fe_3Si film on GaAs

search for a magnetically dead layer





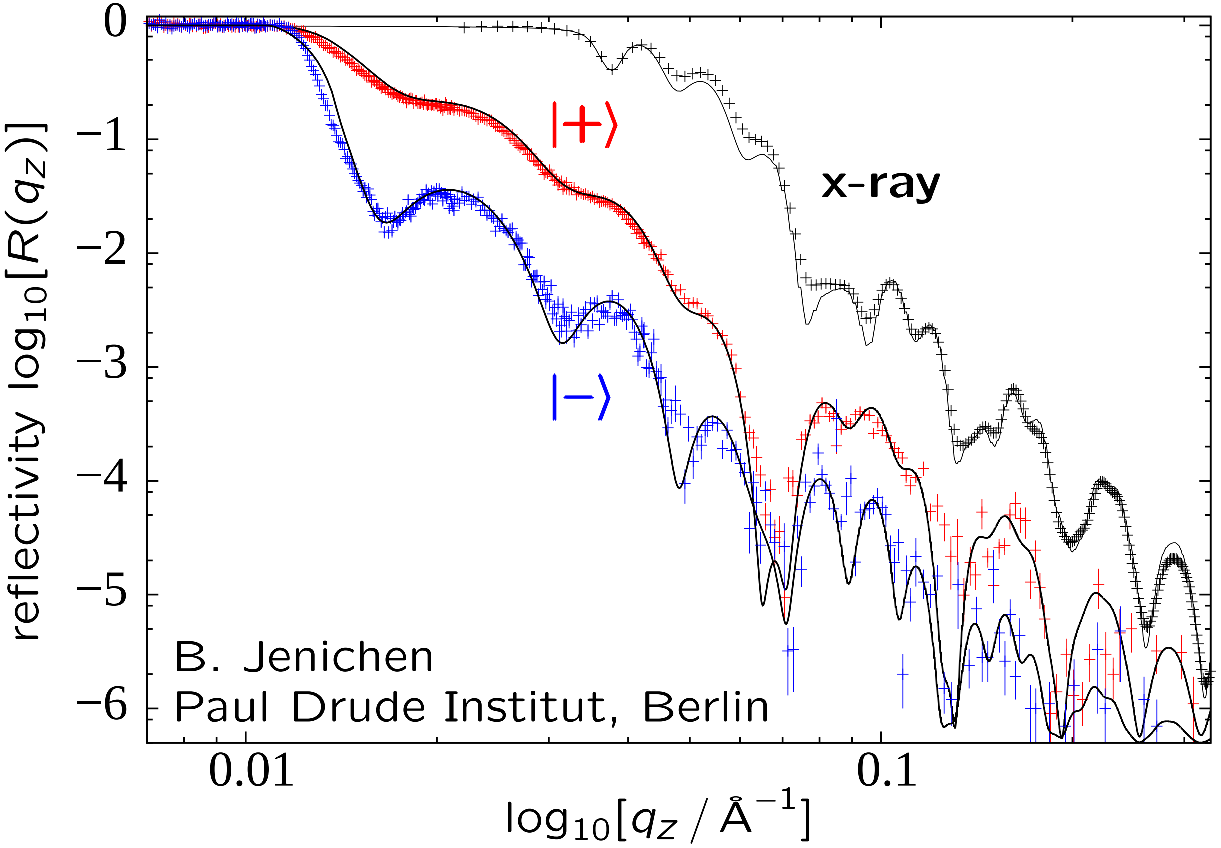
sample size: $5 \times 5\,\text{mm}^2$

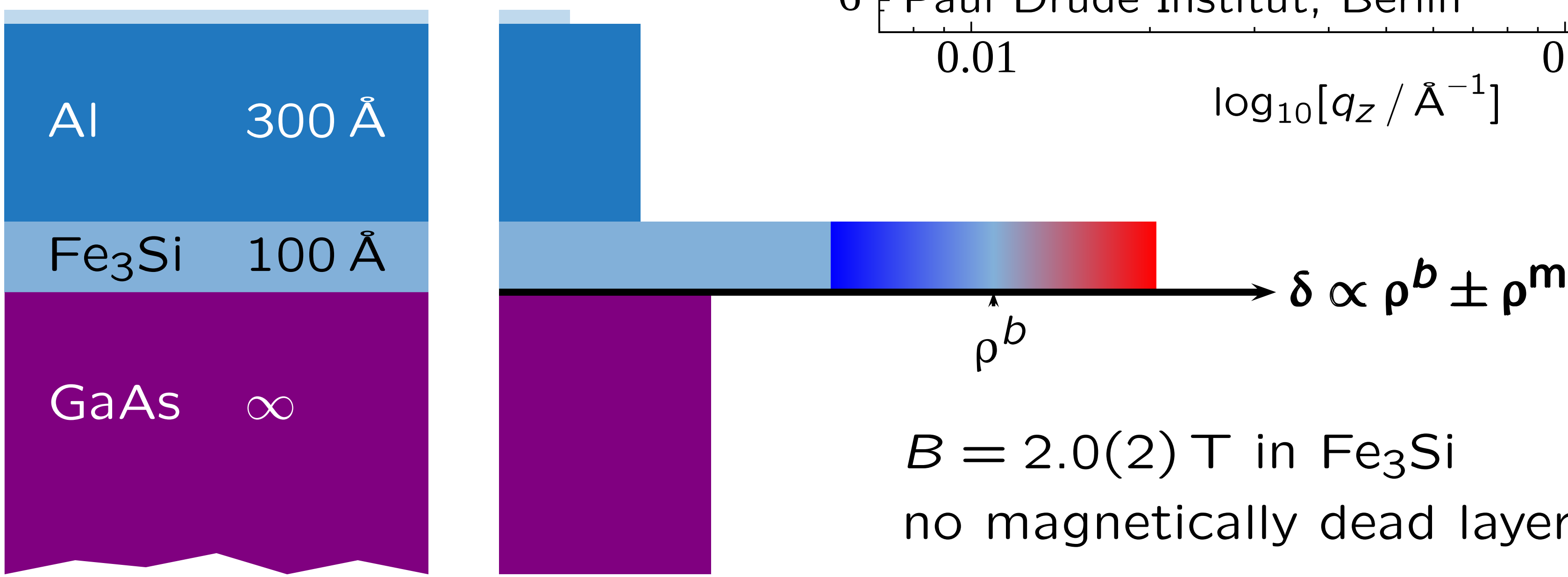
measurement time: 24 h neutron

1 h x-ray

Fe_3Si film on GaAs

search for a magnetically dead layer





$B = 2.0(2)$ T in Fe_3Si

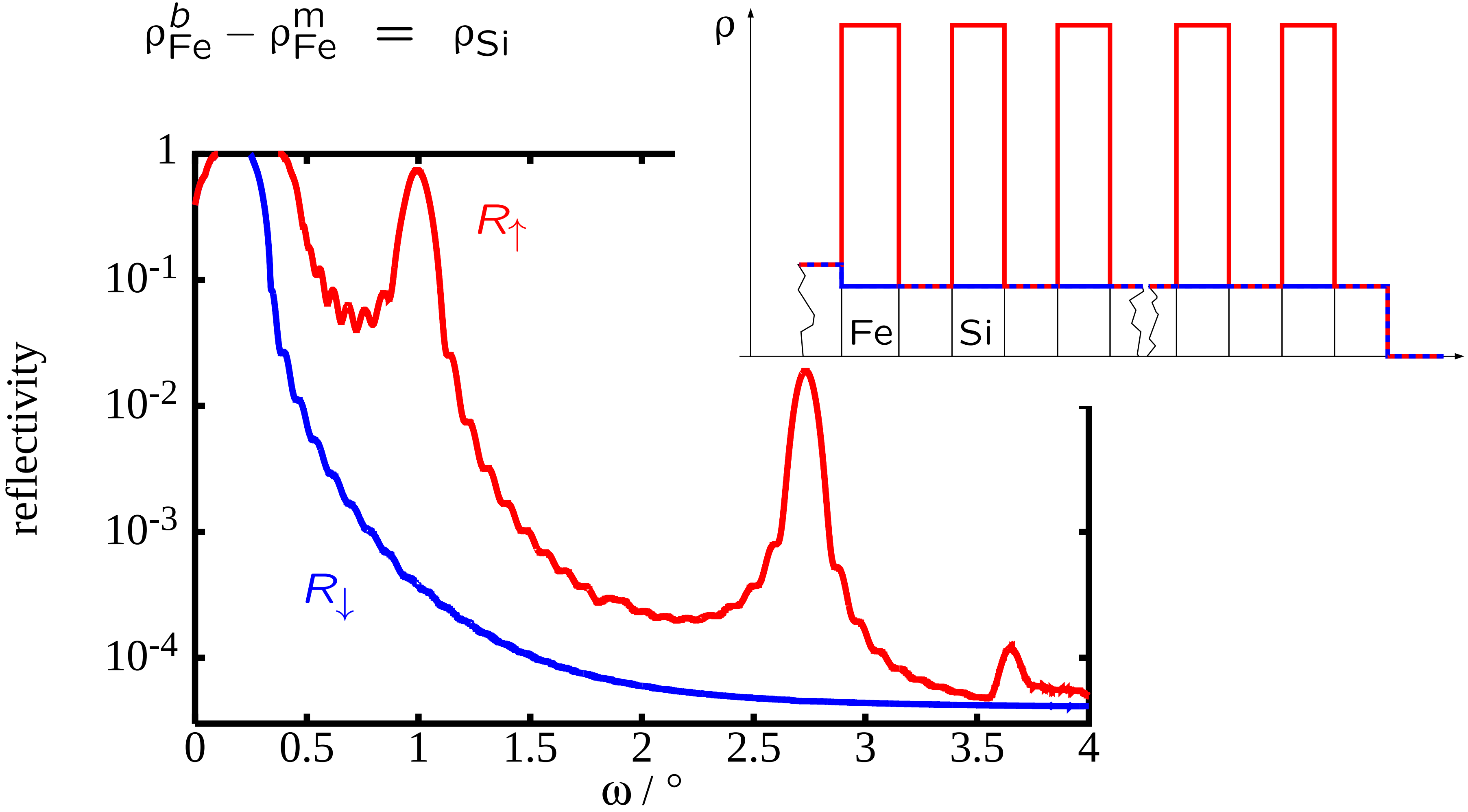
no magnetically dead layer detectable

Fe/Si multilayer

ideal case:

$$\rho^{b}_{\mathrm{Fe}} + \rho^{\mathrm{m}}_{\mathrm{Fe}} \gg \rho_{\mathrm{Si}}$$

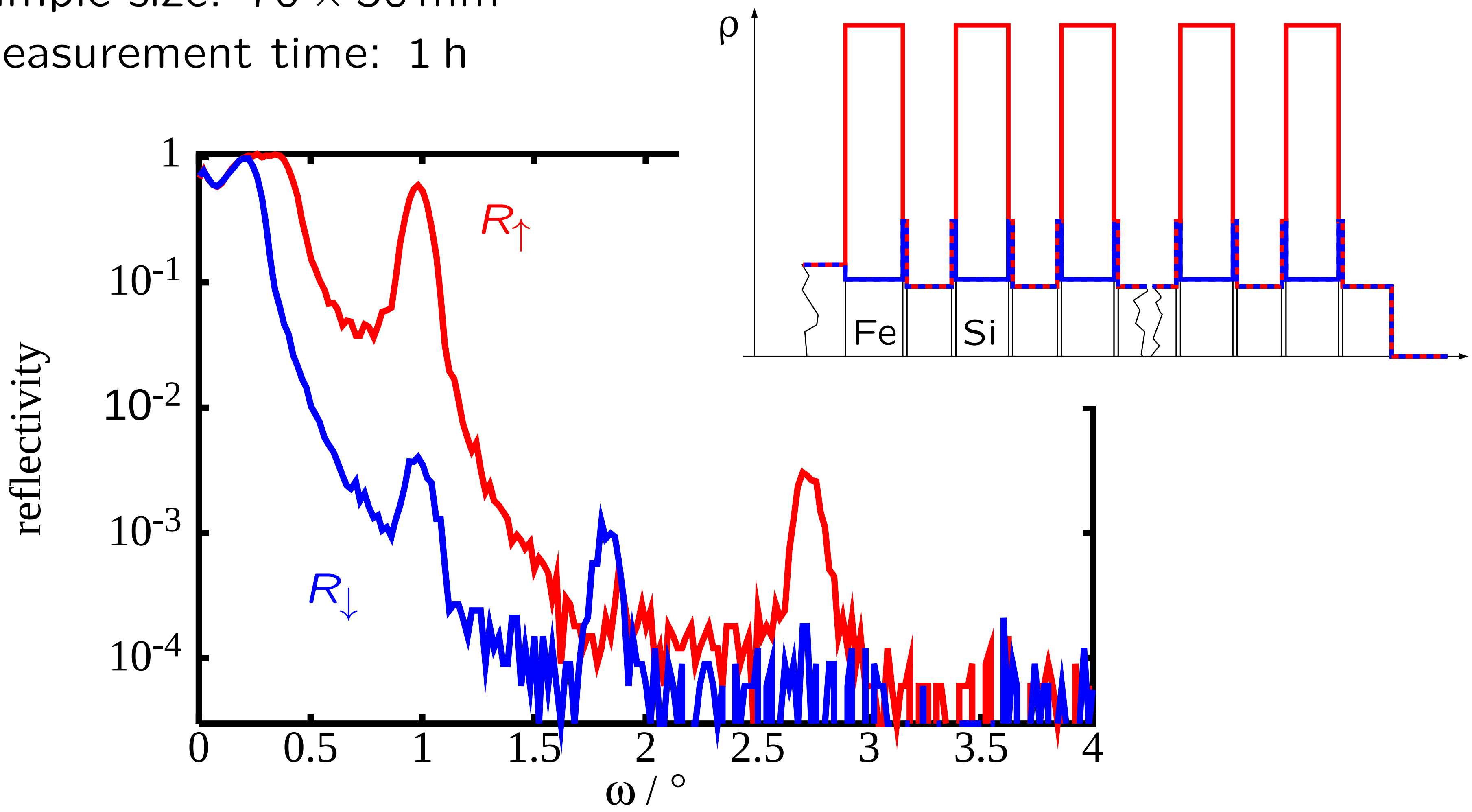
$$\rho^{b}_{\mathrm{Fe}} - \rho^{\mathrm{m}}_{\mathrm{Fe}} = \rho_{\mathrm{Si}}$$



Fe/Si multilayer

reality: interdiffusion leads to 5 Å thin magnetically dead Fe : Si layers

sample size: $70 \times 50\,\mathrm{mm}^2$
measurement time: 1 h

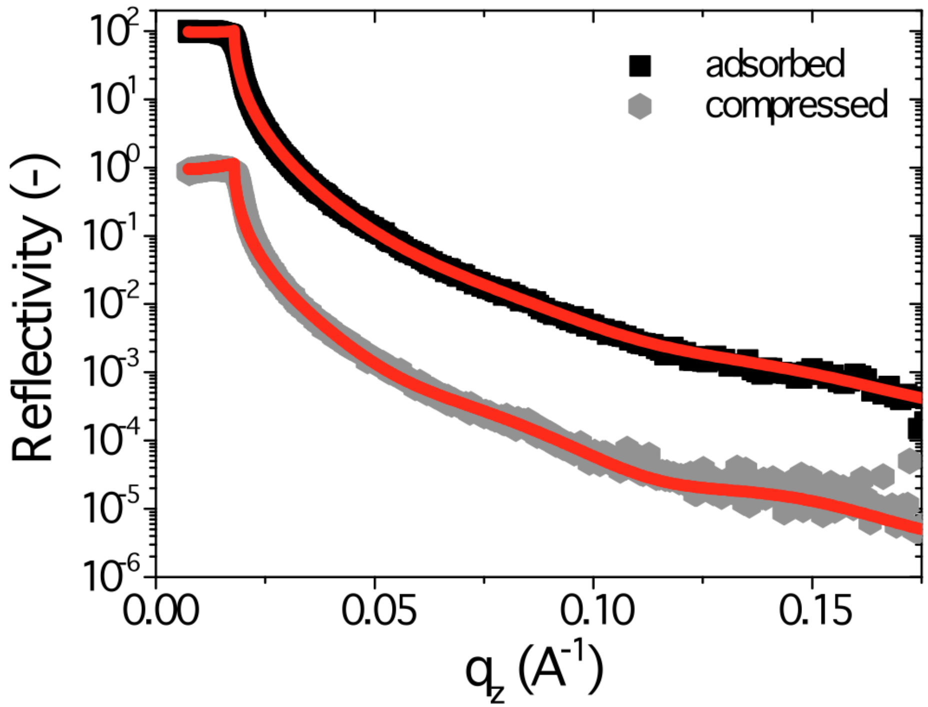


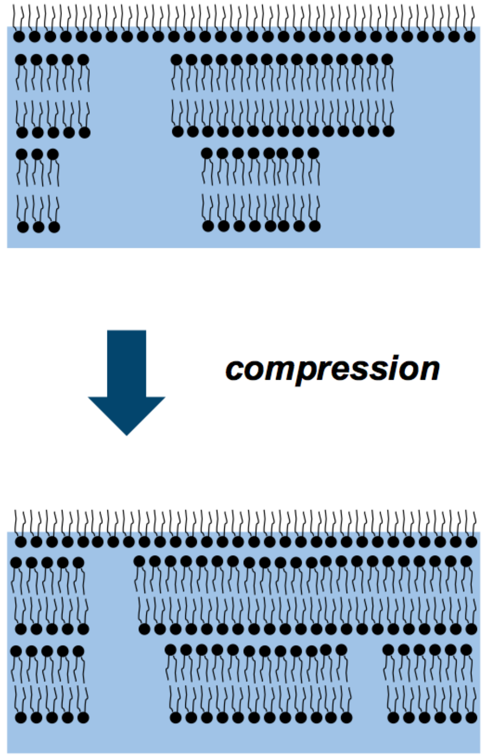
compression of self-organising polyglycerol-ester films

H_2O substituted by D_2O

$\Rightarrow$ strong contrast between solvent and film (essentially $[CH_2]_n$)

$\Rightarrow$ *high* critical edge





constant film thickness

laterally more homogeneous

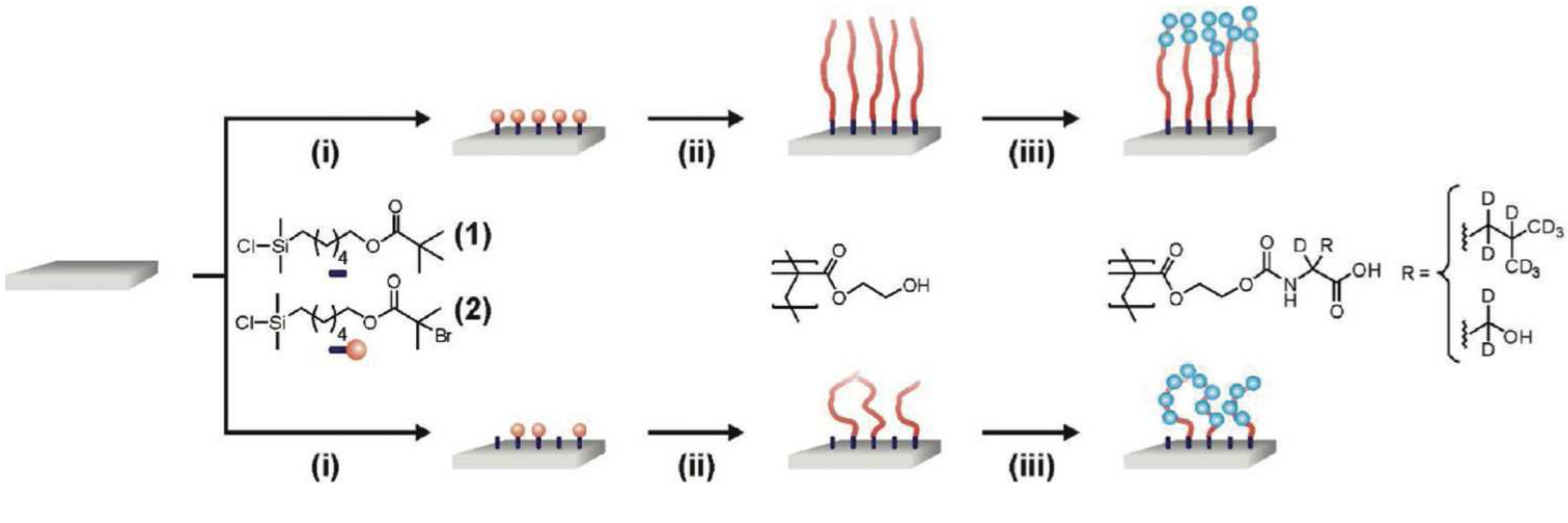
$\Rightarrow$ less *roughness*

$\Rightarrow$ lower damping of $R(q_z)$

C. Curschellas, IACIS, Sendai, 2012

polymer bruches applications:
- anti-fouling color
- coation within ball bearings
- **matrix for chemical sensors**

where are the functional groups located?



substrate activation polymer growth modification

Schüwer, Macromolecules 44, 6868-6874 (2011)

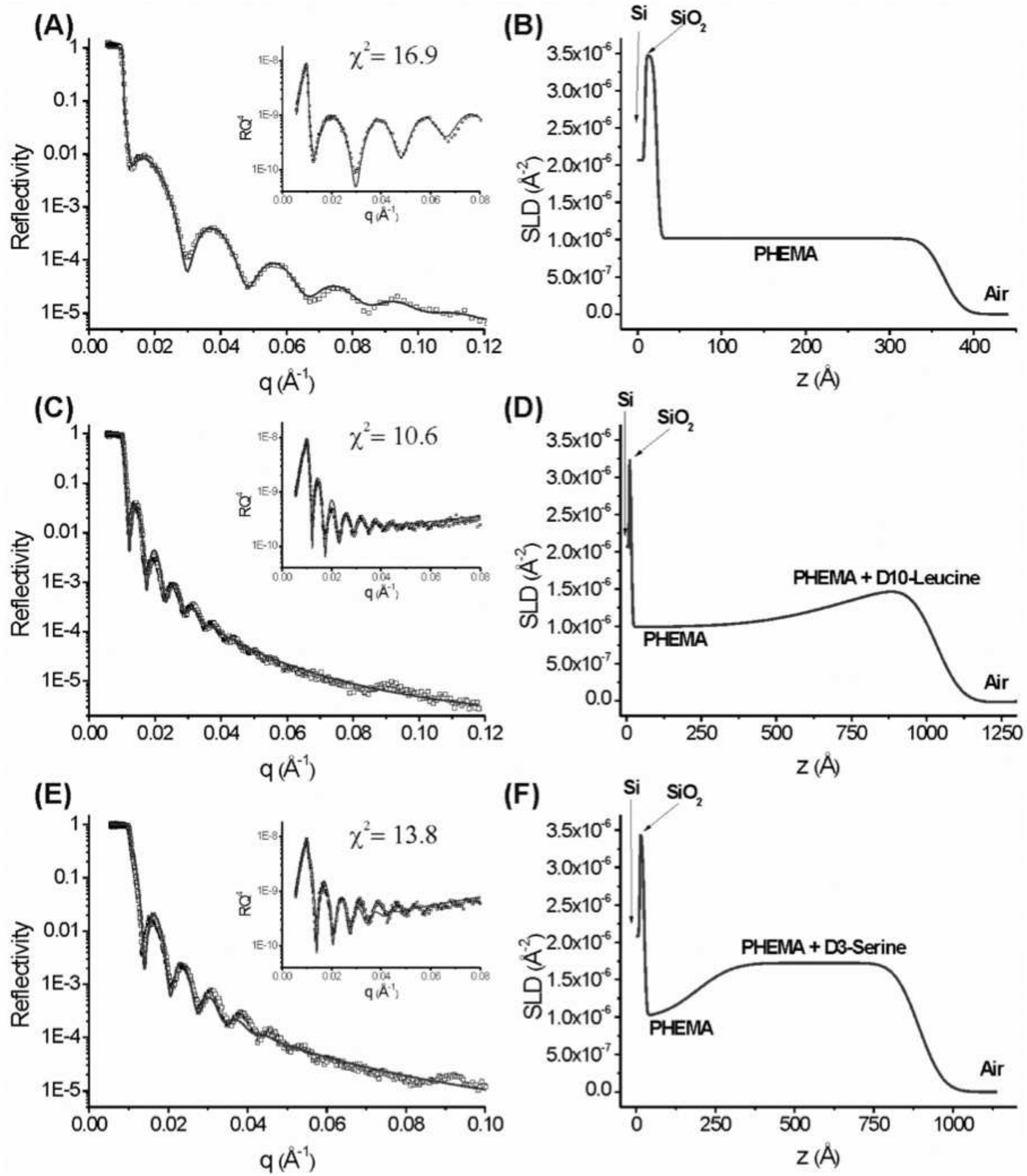
polymer brushes

location of functional groups

341 Å
non-functionalised

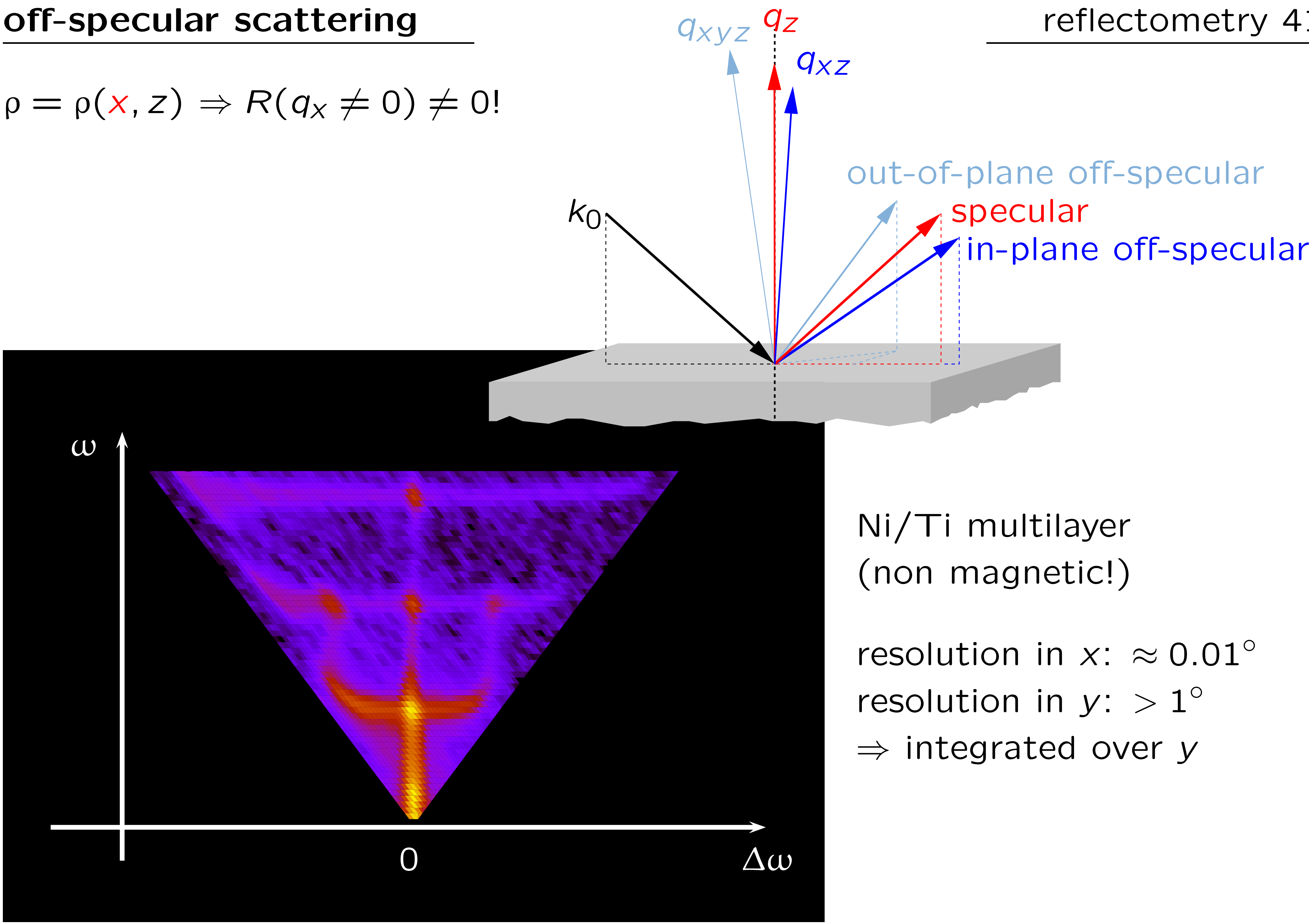
1016 Å
leucine functionalised

867 Å
serine functionalised



off-specular scattering

$$\rho = \rho({\color{red}x}, z) \Rightarrow R(q_x \neq 0) \neq 0!$$



Ni/Ti multilayer
(non magnetic!)

resolution in x: $\approx 0.01^\circ$
resolution in y: $> 1^\circ$
$\Rightarrow$ integrated over y

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- . . . derivation
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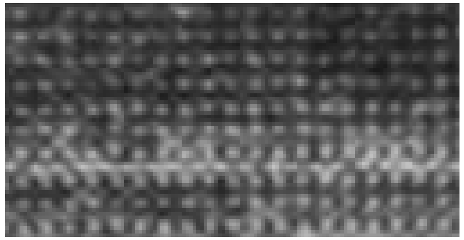
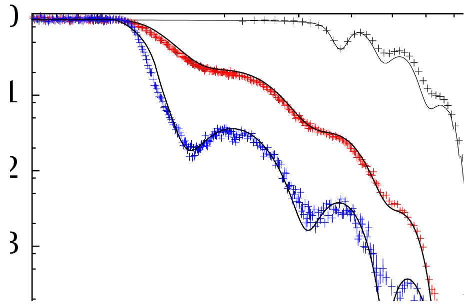
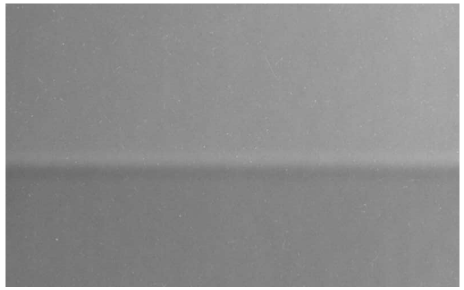






total reflection and refraction change beam direction

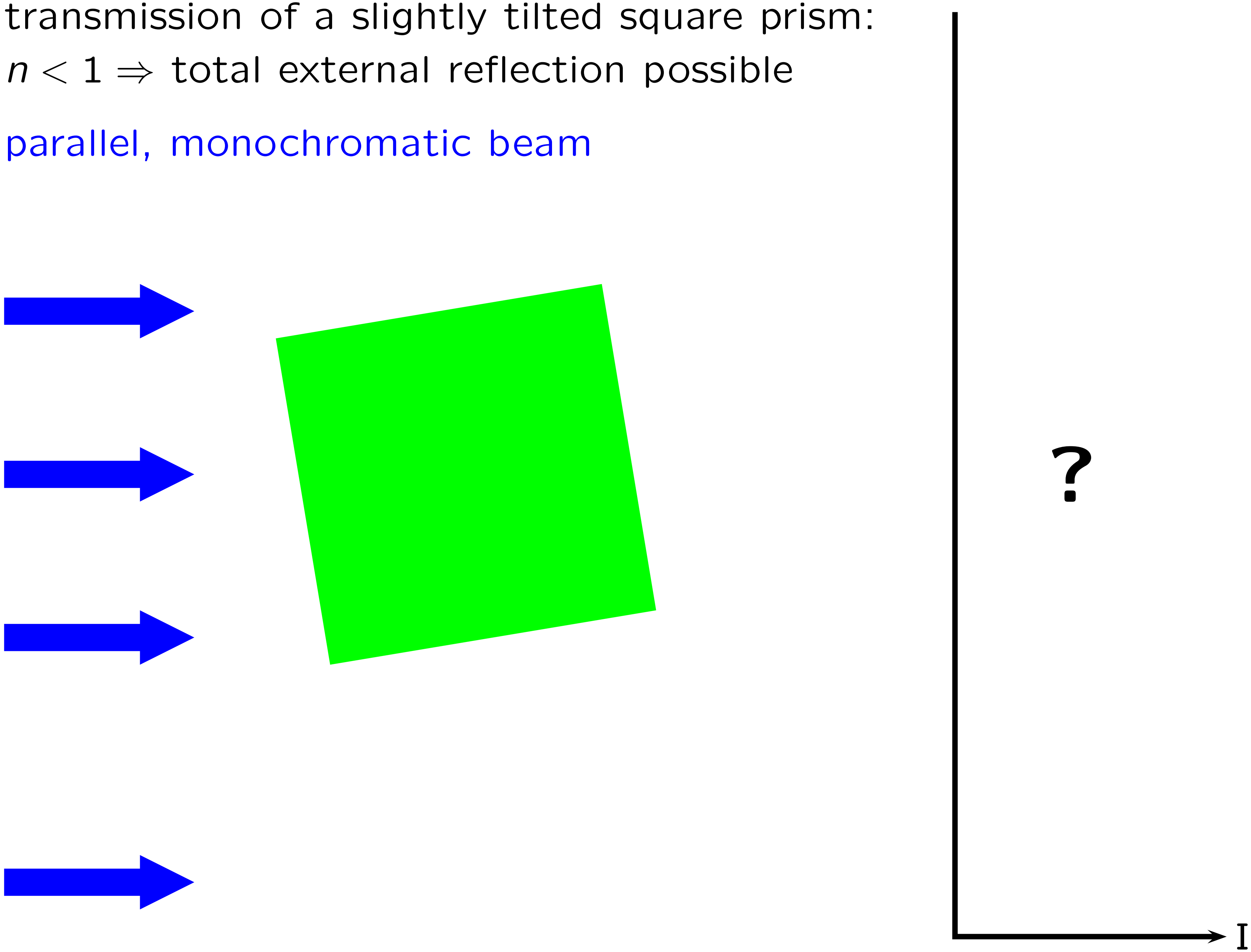
$\Rightarrow$ important for *large* sample-detector distances

also (optically) rough interfaces show significant total reflection!

transmission of a slightly tilted square prism:

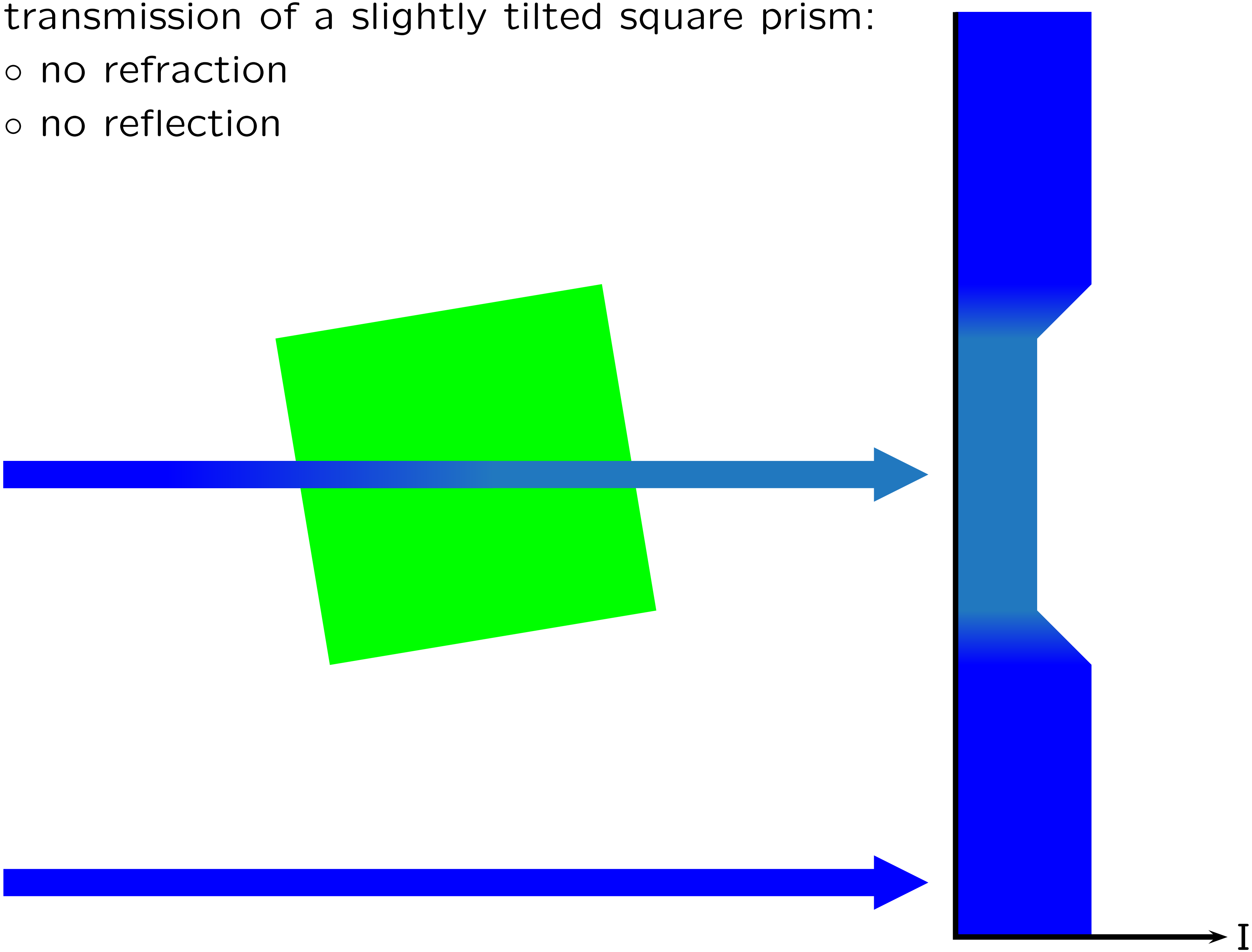
$n < 1 \Rightarrow$ total external reflection possible

parallel, monochromatic beam



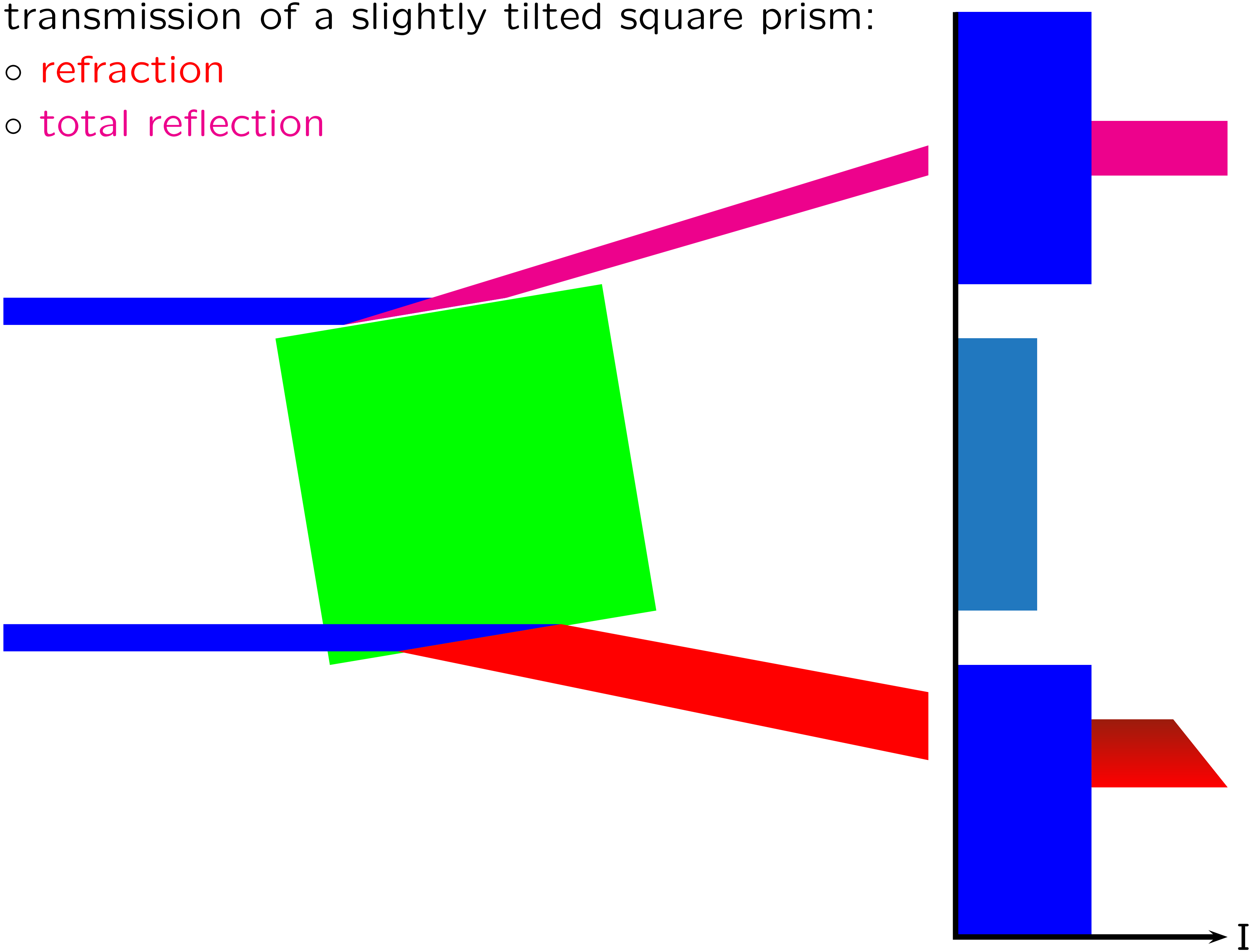
transmission of a slightly tilted square prism:

- ◦ no refraction
- ◦ no reflection



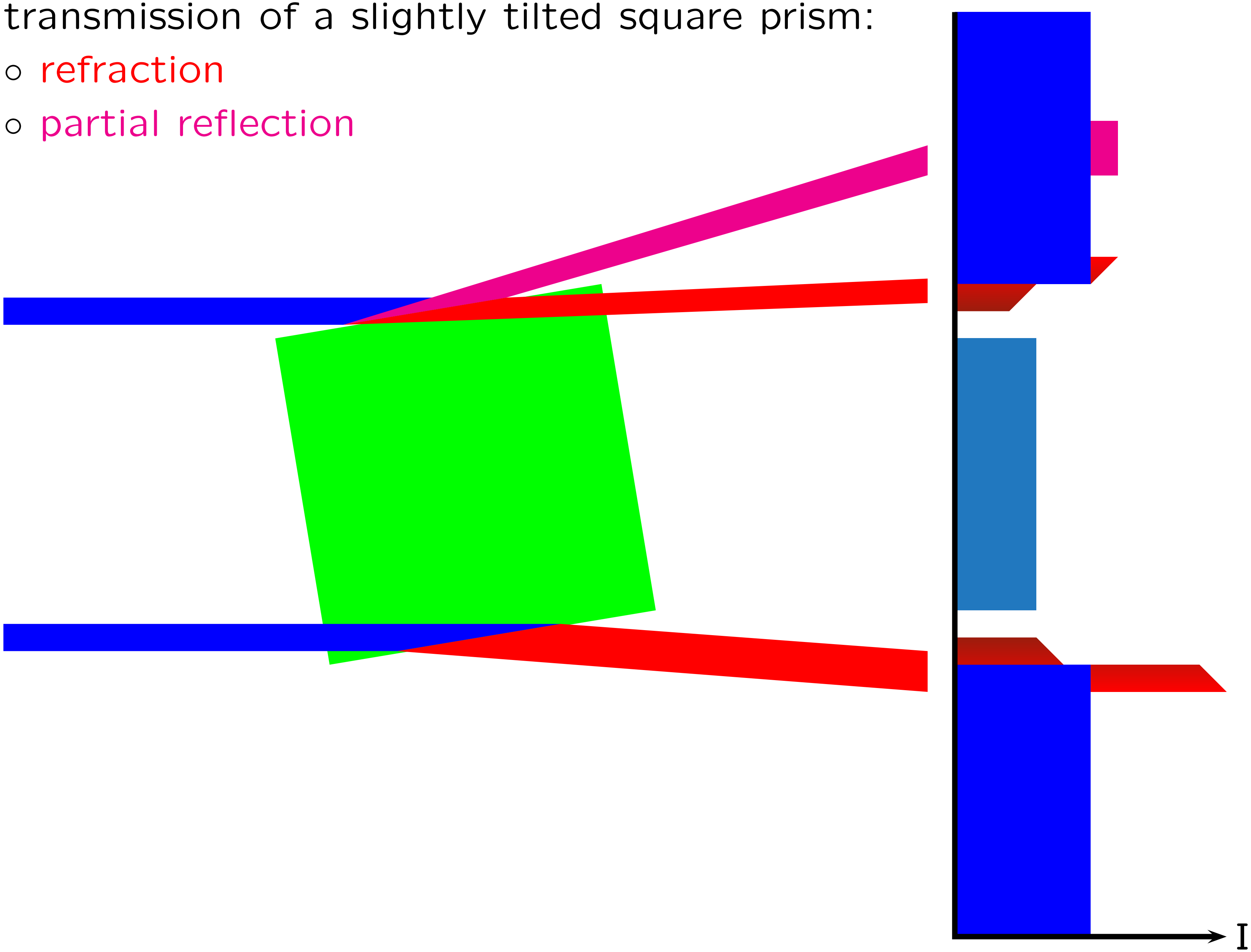
transmission of a slightly tilted square prism:

- ○ refraction
- ○ total reflection



transmission of a slightly tilted square prism:

- refraction
- partial reflection

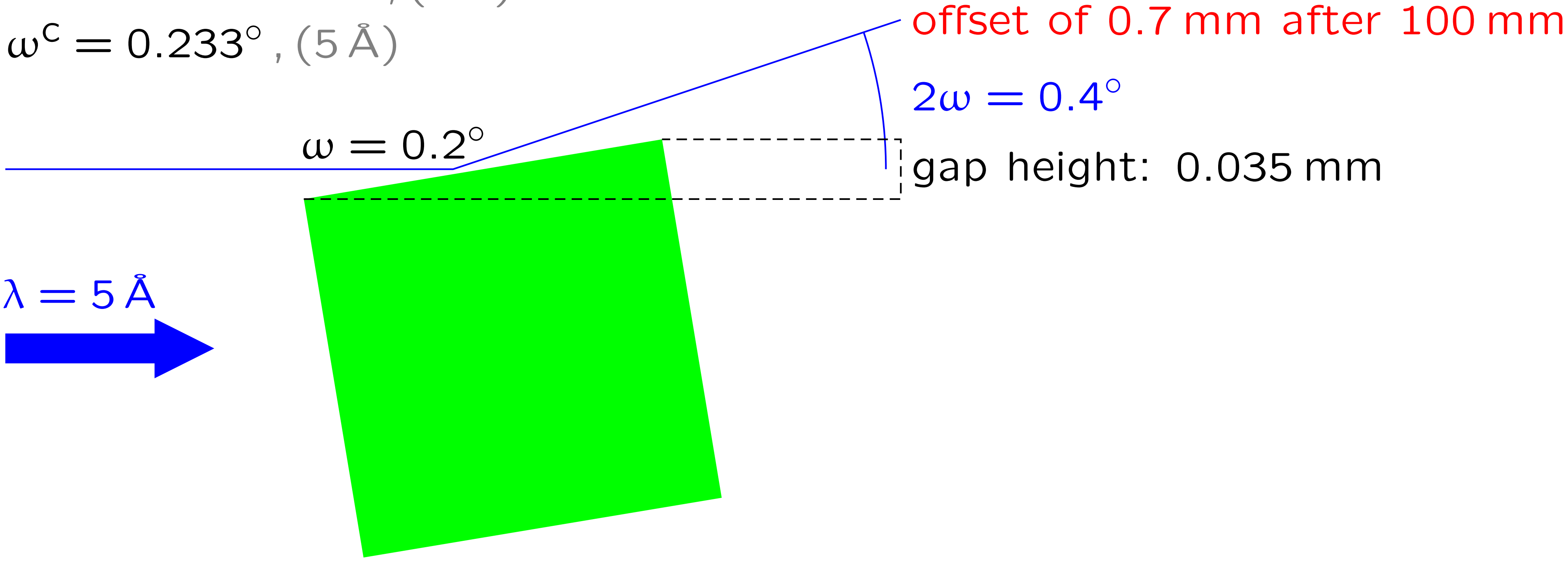


transmission of a slightly tilted square prism: some numbers

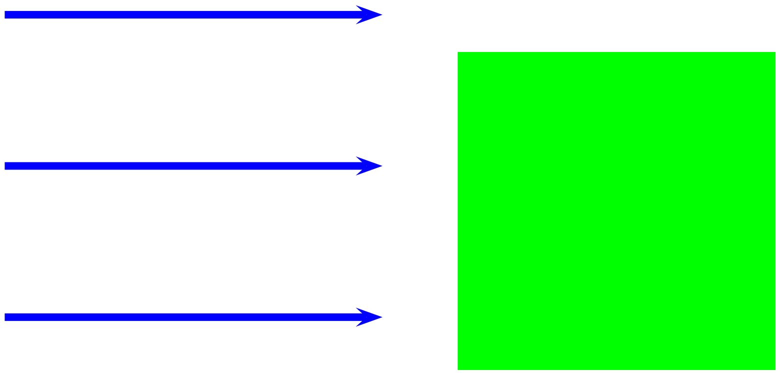
Al prism with $\varnothing = 10 \times 10\,\mathrm{mm}^2$

$n = 1 - 8.3 \cdot 10^{-6}$, (5 Å)

$\omega^{c} = 0.233°$, (5 Å)

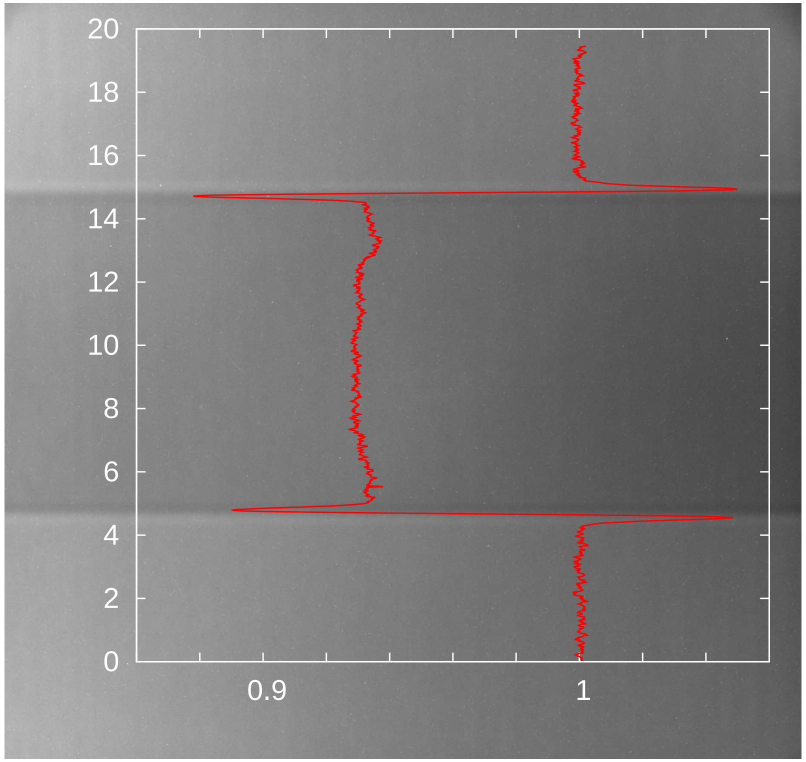


$\Rightarrow$ reflection (and refraction) can lead to detectable features like *halos* or *shadows* measured transmission (Eberhard Lehmenn, PSI)



$\lambda \in [1.8, 5]$ Å   Al   100 mm

$\Delta\omega \approx 0.1^\circ$ $10 \times 10\,\mathrm{mm}^2$



Al cube has not perfectly flat and parallel surfaces

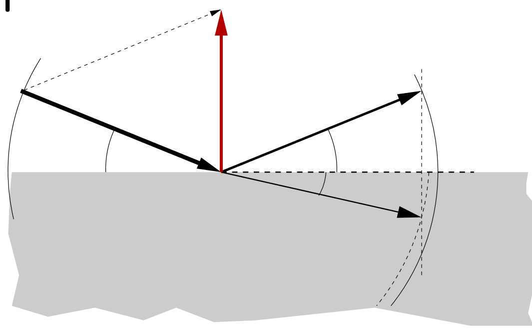
$\Rightarrow\ \omega = 0 \pm \Delta\omega_{\mathrm{beam}} \pm \Delta\omega_{\mathrm{surface}}$

reflectometry probes depth-profile of some potential

averages laterally

$\Rightarrow$ ideal for layered systems

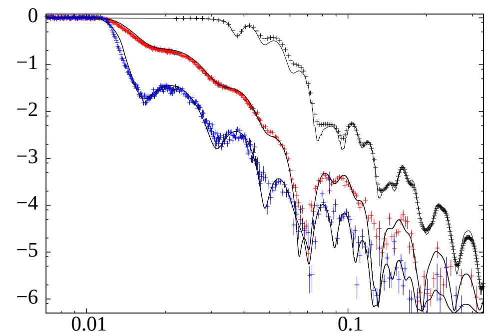
data analysis by modelling



with neutrons resolution: atom to sub-μm

isotope selective

detects in-plane magnetic induction

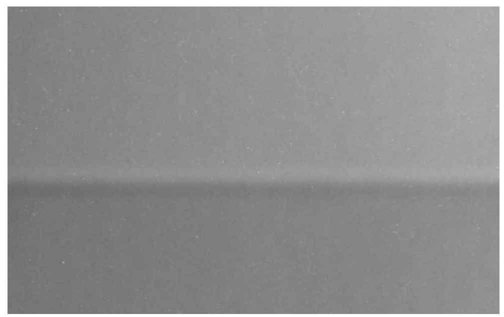


with x-rays resolution: atom to sub-μm

detects electron density

. . . in resonance detects magnetic states of atoms

radiography might be affected !!!



reflectometry, in general :

J. Daillant, A. Gibaud:
X-ray and Neutron Reflectivity
Lect. Notes Phys. 770 (Springer 2009)

U. Pietsch, V. Holý, T. Baumbach:
High-Resolution X-Ray Scattering
(Springer 2004)

. . . on magnetic systems

F. Ott:
Neutron scattering on magnetic surfaces
C. R. Physique **8**, 763-776 (2007)

. . . using resonant x-rays

S. Brück:
Magnetic Resonant Reflectometry on Exchange Bias Systems
Dissertation, Stuttgart 2009